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(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 February 2003 (13.02.2003)

PCT

(10) International Publication Number
WO 03/011917 A1

(51) International Patent Classification⁷: **C08F 8/18**

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(21) International Application Number: PCT/US02/11548

(22) International Filing Date: 9 April 2002 (09.04.2002)

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(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/308,893 31 July 2001 (31.07.2001) US
60/316,611 31 August 2001 (31.08.2001) US

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier applications:

US 60/308,893 (CON)
Filed on 31 July 2001 (31.07.2001)
US 60/316,611 (CON)
Filed on 31 August 2001 (31.08.2001)

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

— with international search report

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF CURING ELASTOMERS

(57) Abstract: Embodiments of the present invention include a composition of, and a method of curing, an elastomer such as an unsaturated elastomer or a substituted phenylic elastomer. In one embodiment, the elastomer is a brominated poly(isobutylene-co-4-methylstyrene) elastomer ("BIMS"), and in another it is butyl-type rubber or other unsaturated rubber. The composition and method of curing the elastomer includes blending an inducer compound with at least one elastomer and at least one cure agent. The inclusion of the inducer compound advantageously improves the cure properties of the elastomer or elastomer blend. The inducer compound is a compound capable of transferring a halogen species to another agent such as an electrophilic moiety. In one embodiment of the invention, the inducer compound is a mono-, di- or tri- (substituted)aryl methyl halide, such that the halide is a bromide or chloride.

WO 03/011917 A1

TITLE: METHOD OF CURING ELASTOMERS**FIELD OF INVENTION**

5 The present invention relates to a composition of, and method of curing, an elastomer or blend of elastomers, in particular, to curing vinyl aromatic-containing polymers useful in, for example, vehicle tires, air barriers and damping pads.

BACKGROUND OF THE INVENTION

10 Elastomers such as, for example, unsaturated polymers or polymers incorporating substituted phenyl groups, are commonly used in compositions for articles where abrasion resistance, impact absorption and flexibility are desirable features. Such elastomers should be processable at a relatively low temperature while in its green (uncured) state, and allow a rapid cure to a state that gives the final elastomer its advantageous properties as a finished article. Such is the case
15 in the manufacture of automobile and airline tires, where the elastomeric composition must first be processed (*e.g.*, flow, extrusion, manipulation, shaping, etc.), followed by heating to cause a cure. In processing, heat can be generated which may lead to the undesirable consequence of premature curing or compound viscosity increases. High throughput rates in processing are particularly likely to
20 generate heat, and thus undesirable premature curing. Thus, improvements in the cure chemistry of these elastomers are not only of interest for purposes of manufacturing cost-effectiveness, improvements in the final properties of the cured elastomers are also of interest.

25 Cure chemistry development is a non-trivial process critical to isobutylene-based elastomer product development. Independent control of scorch time, cure rate, and final cure state is highly desirable, yet elusive. The curing of an elastomeric polymer, induced by such techniques as radiative heating, typically takes place in three stages: an induction stage, a curing or crosslinking stage, and
30 undesirably, a reversion stage. These steps are described further in RUBBER TECHNOLOGY 105-133 (Maurice Morton, ed., Chapman & Hall 1995). The induction period is described as a "scorch time", and is the time, at the

vulcanization temperature, at which no measurable crosslinking (measured as an increase in viscosity) occurs. Following the induction stage, crosslinking of the polymer then proceeds at a relatively rapid rate until the chemical agents used to cause the crosslink are depleted, and/or the crosslink sites on the polymer are depleted. Such is described in greater detail in RUBBER TECHNOLOGY 113-133 (Maurice Morton, ed., Chapman & Hall 1995). Elastomer curing is of great importance in multi-component articles such as tires, as described by *Waddell et al.* in THE VANDERBILT RUBBER HANDBOOK 596-621 (R.T. Vanderbilt Company, Inc. 1990). Desirably, the scorch time (often referred to as "scorch safety") at a desirable processing temperature should be long enough to allow flow and manipulation of the elastomer prior to curing.

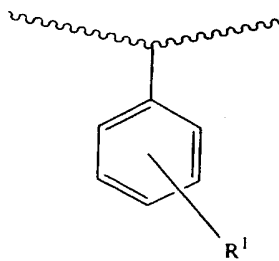
The final cure state of a polymer or elastomer impacts the physical properties and morphology of elastomer formulations. However, a continuing problem in the cure chemistry of many polymers is that these various properties are highly correlated. When one property changes favorably, another property may change to a disadvantage. For example, it is generally known that long scorch times are accompanied by slow cure rates. Yet, a longer scorch time is desirable to facilitate extrusion of a sidewall component without premature crosslinking. Yet, it is desirable for the same compound to have a high cure rate once incorporated into an uncured tire. Unfortunately, changing one property often leads to an undesirable change to another property.

Cure systems have been disclosed for phenylic-type elastomers, such as in US 5,504,164, US 5,512,638, 5,332,787, 6,051,653, 5,656,694 and EP 0 363 208, and as disclosed by *Frechet et al.*, 66 RUBBER CHEMISTRY AND TECHNOLOGY 98-108 (1992) and *Bielski et al.*, 31 JOURNAL OF POLYMER SCIENCE: PART A: POLYMER CHEMISTRY 755-762 (1993). So called sulfur cure additives have been disclosed in US 4,496,683 to cause a cure in diene rubbers, and cure systems for halogenated butyl-type rubbers are known. But none of these references discloses a method of decoupling the various cure properties, especially in halobutyl-type elastomers and phenylic elastomers. What would be desirable is a method of

controlling, for example, scorch time, independently from the final cure state and other cure parameters.

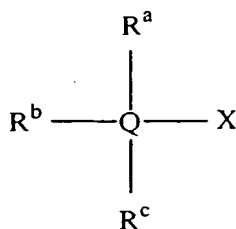
SUMMARY OF THE INVENTION

5 The present invention is a composition of, and a method of curing, elastomers. Examples of elastomers useful in the method of the invention include any unsaturated elastomer such as butyl-type rubber, and/or substituted phenylic elastomers. The phenylic elastomer has at least one monomer unit represented in the following structure, the jagged line referring to the polymer backbone:



10 wherein R^1 is selected from halogen, alkyl, halogenated alkyl, aryl, halogenated aryl, hydroxyl, $-OR^2$, halogenated $-OR^2$, $-COOR^2$, or halogenated $-COOR^2$, wherein R^2 is an alkyl, substituted alkyl, aryl, or substituted aryl. In one
15 embodiment, the substituted phenylic elastomer is a brominated poly(isobutylene-*co*-4-methylstyrene) polymer ("BIMS"). Non-limiting examples of elastomers useful in the invention include any unsaturated elastomer or substituted phenylic
20 elastomer such as poly(isobutylene-*co*-4-methylstyrene) polymer, halogenated poly(isobutylene-*co*-4-methylstyrene) polymer, butyl rubber, poly(styrene-*co*-butadiene), polyisoprene, polybutadiene, halogenated butyl rubber, and
25 halogenated star-branched butyl rubber, polysulfide, nitrile rubber, propylene oxide polymers, and mixtures thereof. Other elastomers and additives may also be blended with the curable elastomer as part of the overall composition, and more than one elastomer may be present in the composition or useful in the method of curing multiple elastomers in a blend.

The composition and method of curing the elastomer includes blending an inducer compound with the elastomer. The inclusion of the inducer compound advantageously improves the cure properties of the elastomer. The inducer compound is a compound capable of transferring a halogen species to a secondary agent such as the elastomer or a cure agent such as a metal oxide, metal carboxylate, or other suitable electrophile. In one embodiment, the inducer compound is a compound represented by the following structure:



wherein Q is carbon, silicon, or germanium, X is a halogen, and R^a , R^b and R^c are the same or different and are selected from hydrogen, a C_1 to C_{26} alkyl, a C_1 to C_{26} substituted alkyl, aryl, or substituted aryl. In one embodiment, Q is carbon, and X is chlorine, bromine, or iodine, and at least one of R^a , R^b and R^c are substituted aryl groups. Non-limiting examples of inducer compounds include benzyl bromide (α -bromotoluene), 1-bromonaphthalene, 4-bromobenzoic acid, methyl α -bromophenylacetate, triphenylmethylbromide (bromotriphenylmethane), 4-bromomethylbenzophenone, brominated vegetable oil, 2-ethylhexylbromide, bromomethyl phenyl sulfone, 4-(bromomethyl)phenylacetic acid, 4-(trifluoromethyl)benzyl bromide, α^2 -chloroisodurene, 2-(chloromethyl)anthraquinone, and 2,4-bis(trifluoromethyl)benzyl bromide, and mixtures thereof.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a graphical representation of data from Example B, plotting the scorch time (s_1 , 135°C) as a function of the cure time (T_{90} , 170°C) for various inducers;

Figure 2 is a graphical representation of data from Example B, plotting the peak rate as a function of the cure state (MH-ML), at 170°C for various inducers;

Figure 3 is a graphical representation of data from Example B, plotting the scorch time (s1, 135°C) as a function of the cure state (MH-ML), at 170°C for various inducers;

Figure 4 is a graphical representation of data from Example C, plotting the scorch time (s1, 135°C) as a function of the cure time (T90, 170°C) for various inducers;

Figure 5 is a graphical representation of data from Example C, plotting the peak rate as a function of the cure state (MH-ML), at 170°C for various inducers; and

Figure 6 is a graphical representation of data from Example C, plotting the scorch time (s1, 135°C) as a function of the cure state (MH-ML), at 170°C for various inducers.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a composition of, and a method of curing, at least one elastomer, or a blend of elastomers that allows for improved control of the scorch time, cure rate, and final cure state. In one embodiment, the at least one elastomer is a substituted phenylic elastomer such as poly(isobutylene-co-4-methylstyrene). Alternatively, the elastomer is a butyl-type rubber or other unsaturated rubber. In yet another embodiment, the composition of the invention, and method of curing, includes a blend of two or more elastomers such as a butyl-type rubber and a phenylic elastomer, or two butyl-type rubbers, etc. The method includes the use of an inducer compound that possesses a halogen moiety that is readily dissociatable or subject to substitution.

The invention also includes a composition comprising an elastomer and an inducer compound. The composition may also include other components such as at least one cure agent, a filler and/or additional elastomers such as polybutadiene or natural rubber in other embodiments. For example, the composition of the invention may include a blend of a substituted phenylic elastomer and a butyl-type rubber, a cure agent including a metal oxide or metal ligand complex and a non-halogenated phenolic resin, a filler, and an inducer compound. As used herein, the term "butyl-type" rubber or elastomer refers to a polymer having isoolefin monomer units, and may include multiolefin monomer units.

The terms "cure" and "vulcanize", as used herein, are used interchangeably, and refer to both crosslinking reactions and the process used to achieve crosslinking of polymer chains within an elastomer composition.

The term "phr" is parts per hundred rubber, and is a measure common in the art wherein components of a composition are measured relative to the total weight of elastomer(s), based upon 100 parts by weight of the elastomer or elastomers.

As used herein, in reference to Periodic Table "Groups", the new numbering scheme for the Periodic Table Groups are used as in HAWLEY'S CONDENSED CHEMICAL DICTIONARY 852 (13th ed. 1997).

The term "elastomer", as used herein, refers to any polymer or composition including a polymer that can be cured by any means, and in particular refers to any polymer having at least one functional unit that is capable of causing or influencing a cure intermolecularly, and/or intramolecularly. The term "elastomer" may be used interchangeably with the term "rubber" as used herein, and is consistent with the definition in ASTM 1566.

The term "unsaturated elastomer", as used herein, refers to any polymer containing at least one carbon-carbon double bond either in the backbone of the polymer or as a functional group pendant on the backbone. So called "diene" elastomers are unsaturated elastomers as the term is used herein. The
5 unsaturated elastomer may be a copolymer or homopolymer, and is not limited by the identity of the monomers used to form the polymer. The term "butyl-type" elastomer or rubber refers to any polymer incorporating an olefin or isoolefin derived unit into the polymer, and may also be an unsaturated elastomer as the term is used herein when copolymerized with a multiolefin or
10 other monomer unit that allows for a carbon-carbon double bond to remain in the polymer.

The term "substituted phenylic elastomer" or "phenylic elastomer", as used herein, refers to a class of polymers described generally as incorporating
15 within the polymer backbone at least one monomer unit having a substituted aryl, preferably phenyl, moiety.

The term "cure agent" refers to a compound that is used to cause a cure of the elastomer of the invention. The cure agent can include such compounds
20 known in the art as metal oxides, metal ligand complexes, and phenolic resins used to cause a cure in elastomeric compositions.

As used herein, the terms "substituted phenyl", "substituted naphthyl" and "substituted aryl" mean phenyl, naphthyl and aryl groups, respectively, substituted
25 by at least one substituent selected from, for example, halogen (chlorine, bromine, fluorine, or iodine), amino, nitro, sulfoxy (sulfonate or alkyl sulfonate), thiol, alkylthiol, and hydroxy; alkyl, straight or branched chain having 1 to 20 carbon atoms; alkoxy, straight or branched chain alkoxy having 1 to 20 carbon atoms, and includes, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy,
30 secondary butoxy, tertiary butoxy, pentyloxy, isopentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, and decyloxy; haloalkyl, which means straight or branched chain alkyl having 1 to 20 carbon atoms which is substituted by at least one

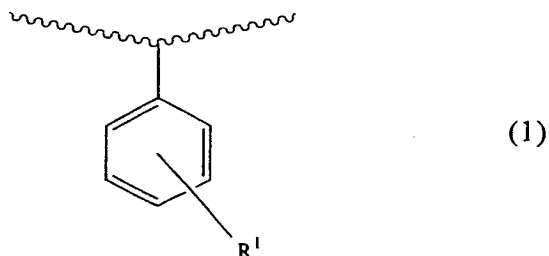
halogen, and includes, for example, chloromethyl, bromomethyl, fluoromethyl, iodomethyl, 2-chloroethyl, 2-bromoethyl, 2-fluoroethyl, 3-chloropropyl, 3-bromopropyl, 3-fluoropropyl, 4-chlorobutyl, 4-fluorobutyl, dichloromethyl, dibromomethyl, difluoromethyl, diiodomethyl, 2,2-dichloroethyl, 2,2-diboromethyl, 2,2-difluoroethyl, 3,3-dichloropropyl, 3,3-difluoropropyl, 4,4-dichlorobutyl, 4,4-difluorobutyl, trichloromethyl, 4,4-difluorobutyl, trichloromethyl, trifluoromethyl, 2,2,2-trifluoroethyl, 2,3,3-trifluoropropyl, 1,1,2,2-tetrafluoroethyl, and 2,2,3,3-tetrafluoropropyl. An "aryl" group is any aromatic ring structure such as a phenyl or naphthyl group.

Elastomer

The elastomer useful in the present invention is a polymer, copolymer, terpolymer, interpolymer, or other polymer that is curable by any means known to those skilled in the art. In particular, the at least one elastomer useful in the present invention is any polymer made up of monomer units, at least one monomer unit of which includes a functional group (*e.g.*, a carbon-carbon double bond, dissociatable group, etc.) capable of undergoing a crosslink-type of reaction with another adjacent moiety, either intermolecular or intramolecular. Particularly useful elastomers for the present invention are unsaturated elastomers such as substituted phenylic elastomers and butyl-type rubbers. Non-limiting examples of elastomers useful in the present invention include, for example, butyl rubber, polyisoprene, polybutadiene, halogenated butyl rubbers, halogenated star-branched butyl rubbers, poly(isobutylene-*co*-4-methylstyrene), halogenated poly(isobutylene-*co*-4-methylstyrene), styrene-*co*-butadiene, and other styrene-based elastomers, polysulfide, nitrile rubber, propylene oxide polymers and mixtures thereof. Examples of these and other suitable elastomers and their properties are well known and are disclosed in, for example, THE VANDERBILT RUBBER HANDBOOK 22-262 (R.T. Vanderbilt Company, Inc. 1990), HANDBOOK OF PLASTICS, ELASTOMERS AND COMPOSITES 1.1-1.101 (Charles A. Harper, ed., McGraw-Hill 1992), and RUBBER TECHNOLOGY 1-438 (Maurice Morton, ed., Chapman & Hall 1995).

One embodiment of the elastomer useful in the present invention is any elastomer made up of monomer-derived units, wherein at least one polymerizable monomer-derived unit includes a substituted phenyl $\{(R^1)_n C_6H_{5-n} -\}$ moiety such as styrene, 4-methylstyrene, etc. By polymerizable, it is meant that the monomer should include any moiety that is capable of undergoing polymerization, either by, for example, an anionic or cationic process, radical polymerization process, condensation process, or other suitable process, to form a polymer of the monomer units, which can be the same or different. The value of n in the equation above can range from 1 to 5, and desirably from 1 to 2. By substituted, it is meant that the phenyl moiety has bound, such as by a covalent bond in the ortho, meta, or para positions, any of a number of functional groups R^1 . In a desirable embodiment, the functional group is a leaving group or includes a leaving group, such as defined in, for example, *Morrison and Boyd*, ORGANIC CHEMISTRY 170-184 (Allyn and Bacon, Inc. 5th ed., 1987).

In another embodiment of the invention, the substituted phenylic elastomer is an elastomer having at least one monomer unit such as represented in structure (1):



wherein R^1 is selected from a halogen, preferably bromine or chlorine, alkyl, halogenated alkyl, aryl, halogenated aryl, hydroxyl, $-OR^2$, halogenated $-OR^2$, $-COOR^2$, or halogenated $-COOR^2$, wherein R^2 is an alkyl, substituted alkyl, aryl, or substituted aryl. The R^1 group can be in any of the ortho, meta, or para positions in one embodiment, or in the para position in another embodiment. The term "substituted alkyl" refers to an alkyl group having any of a number of substitutions along its carbon chain including other alkyls, aryls, halogens, hydroxyl groups, or

other suitable moieties, or cyclic alkyls. The term "substituted aryl" refers to any aromatic ring system, such as a benzyl or naphthyl ring, having any number of substitutions along its carbon chain including other alkyls, aryls, halogens, hydroxyl groups, or other suitable moieties, or cyclic alkyls, as described above.

5 The term "alkoxy" refers to any alkyl group having an ether functionality.

In one embodiment, the R_1 group is a C_1 to C_6 halogenated alkyl, and in another embodiment the R_1 group is a C_1 to C_3 halogenated alkyl, wherein the halogen in either instance is selected from the group consisting of chlorine, bromine or iodine. The halogen is bromine in a preferred embodiment.

10

The phenylic elastomer useful in the present invention can be any polymer having at least one polymerizable substituted phenyl unit, the other polymerizable units being any number of monomers such as outlined generally by *M. Rothe* in POLYMER HANDBOOK IV/1-IV/104 (John Wiley & Sons, J. Brandrup, E.H. Immergut & E.A. Grulke, eds., 4th ed., 1999). Examples of suitable substituted phenylic elastomers may include, for example, those disclosed in US 5,567,795 (highly branched polymer of substituted phenyl moiety); US 5,446,124 (substituted aromatic thermoplastics); US 5,304,609 (substituted phenyl group in graft copolymers); US 5,162,445 (functionalized poly(isobutylene-co-styrene) elastomers); US 5,047,470 (substituted styrenes in copolyether-ester elastomers); US 4,950,732 (condensation polymer having substituted phenyl moieties); US 4,933,397 (N-substituted phenyl polybenzimidazole polymers); US 4,767,837 (poly(aryl ether ketone) polymers including substituted phenyl moieties); US 4,755,564 (substituted aryl moiety in graft copolymers); US 4,546,145 (radical polymerizable vinyl polymer having substituted phenyl moieties); and US 4,097,661 (conjugated diolefinic polymers having substituted phenyl moieties).

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In one embodiment of the substituted phenylic elastomer, the monomer unit is a substituted styrene. Any of a number of other monomers may be used to form the substituted phenylic elastomer, including ethylene or C_3 to C_{12} α -olefins; or multiolefins such as a C_4 to C_{14} multiolefin exemplified by isoprene, butadiene,

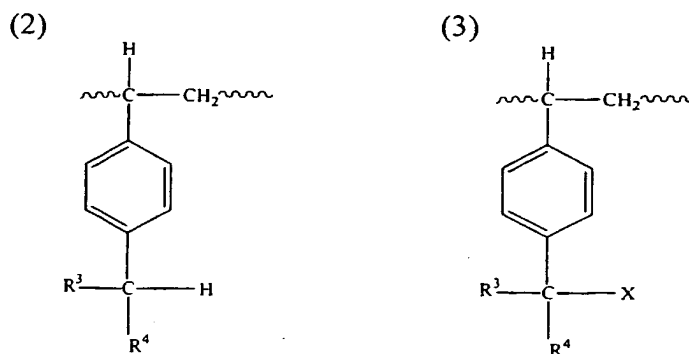
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2,3-dimethyl-1,3-butadiene, cyclopentadiene, myrcene, 6,6-dimethyl-fulvene, hexadiene, and piperylene. In one embodiment, the monomer unit is copolymerized with ethylene or a C₃ to C₈ α -olefin such as propylene, 1-butene, 1-hexene, and isobutylene.

5

In one embodiment, the substituted styrene is 4-alkylstyrene, the substituted styrene comprising at least 80 wt% 4-methylstyrene in one embodiment, and more preferably at least 90 wt% para-substituted (4-substituted). The substituted styrene also includes functionalized interpolymers wherein at least some of the alkyl substituent groups present in the styrene monomer units contain a phenylic halogen or some other functional group. Preferred materials may be characterized as interpolymers containing the following monomer units randomly spaced along the polymer chain:

10



wherein R³ and R⁴ are independently hydrogen, lower alkyl, preferably C₁ to C₇ alkyl and primary or secondary alkyl halides and X is a functional group such as halogen, or other suitable moiety capable of dissociation or susceptible to substitution. In one embodiment, R³ and R⁴ are each hydrogen. Up to about 60 mol% (mole percent relative to the total moles of 4-methylstyrene) of the 4-substituted styrene present in the interpolymers structure may be the functionalized structure (3) above in one embodiment, and in another embodiment from 0.1 to 10 mol%.

20

The functional group X may be halogen, desirably chlorine or bromine, or some other functional group such as carboxylic acids; carboxy salts; carboxy esters, amides and imides; hydroxy; alkoxide; phenoxide; thiolate; thioether; xanthate; cyanide; cyanate; amino and mixtures thereof. These functionalized isomonoolefin copolymers, their method of preparation, methods of functionalization, and cure are more particularly disclosed in US 6,011,120, 5,840,810, 5,821,308, 5,814,708, 5,698,640, 5,670,581 and 5,162,445. Other examples of particularly suitable phenylic elastomers or polymers suitable for the method of the invention are thermoplastic compositions such as disclosed in WO 01/21672 A1, EP 0 542 875 B1, and US 6,028,147.

The copolymer of a C₄ to C₇ isoolefin and a 4-alkylstyrene (poly(isobutylene-co-4-methylstyrene) of the present invention also encompasses terpolymers of a C₄ to C₇ isoolefin, 4-alkylstyrene and halogenated 4-alkylstyrene (halogenated poly(isobutylene-co-4-methylstyrene)). The percentages of 4-alkylstyrene and halogenation can vary widely. Different applications may require dramatically different formulations. Most useful of such functionalized materials are elastomeric random copolymers of isobutylene and 4-methylstyrene containing from 0.5 to 20 mol% 4-methylstyrene based on the total copolymer, wherein up to 60 mol% of the methyl substituent groups present on the benzyl ring contain a bromine or chlorine atom, preferably a bromine atom (4-(bromomethyl)styrene), as well as acid or ester functionalized versions thereof, wherein the halogen atom has been displaced by maleic anhydride or by acrylic or methacrylic acid functionality. Generally, the copolymer will have from 2 wt% to 20 wt% 4-alkylstyrene (preferably 4-methylstyrene) based on the total copolymer. In addition, the copolymer may have from 0.20 mol% to 3.0 mol% of the halogenated monomer unit, such as 4-(bromomethyl)styrene.

In a further embodiment of the poly(isobutylene-co-4-methylstyrene), the 4-alkylstyrene monomer unit, such as 4-methylstyrene, is present from 3 wt% to 15 wt% of the copolymer in one embodiment. In another embodiment, the 4-alkylstyrene is present from 4 wt% to 8 wt% of the copolymer.

When present, the halogenated monomer unit, such as 4-(bromomethyl)styrene, is present from 0.20 mol% to 3.0 mol% of the copolymer in one embodiment, and from 0.50 mol % to 1.5 mol% of the copolymer in another embodiment. In yet another embodiment, the 4-(bromomethyl)styrene is present from 0.5 mol% to 1.0 mol% of the copolymer.

A commercial example of such a halogenated elastomer is brominated poly(isobutylene-co-4-methylstyrene) elastomer ("BIMS"), commercially sold under the tradename EXXPRO™ Elastomers (ExxonMobil Chemical Company, Houston TX) that come in various grades, depending upon, among other things, the desired Mooney Viscosity and level of bromination. Many grades of EXXPRO™ Elastomers exist, non-limiting examples of which include EXXPRO™ 90-10 having 7.5 wt% 4-methylstyrene and 1.20 mol% 4-(bromomethyl)styrene, and EXXPRO™ 89-1 having 5 wt% 4-methylstyrene and 0.75 mol% 4-(bromomethyl)styrene, and other grades listed in Table 2.

Alternatively, the elastomer useful in the present invention may be any unsaturated elastomer such as a butyl-type rubber or a halogenated butyl-type rubber. Useful elastomers are unsaturated butyl rubbers such as copolymers of olefins or isoolefins and multiolefins, or homopolymers of multiolefins. These and other types of elastomers suitable for the invention are well known and are described in RUBBER TECHNOLOGY 209-581 (Maurice Morton ed., Chapman & Hall 1995), THE VANDERBILT RUBBER HANDBOOK 105-122 (Robert F. Ohm ed., R.T. Vanderbilt Co., Inc. 1990), and *Edward Kresge and H.C. Wang* in 8 KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY 934-955 (John Wiley & Sons, Inc. 4th ed. 1993) and are well known in the art. Non-limiting examples of unsaturated elastomers useful in the method and composition of the present invention are poly(isobutylene-co-isoprene), polyisoprene, polybutadiene, polyisobutylene, poly(styrene-co-butadiene), butyl rubber, halogenated butyl rubber, natural rubber, polysulfide, nitrile rubber, propylene oxide polymers, star-branched butyl rubber and halogenated star-branched butyl rubber and mixtures

thereof. Useful elastomers in the present invention can be made by any suitable means known in the art, and the invention is not herein limited by the method of producing the elastomer.

5 One class of useful elastomers for the present invention are so called butyl rubbers. Butyl rubbers are prepared by reacting a mixture of monomers, the mixture having at least (1) a C₄ to C₁₂ isoolefin monomer component such as isobutylene with (2) a multiolefin, monomer component. The isoolefin is in a range from 70 to 99.5 wt% by weight of the total monomer mixture in one
10 embodiment, and 85 to 99.5 wt% in another embodiment. The multiolefin component in one embodiment is present in the monomer mixture from 30 to 0.5 wt% in one embodiment, and from 15 to 0.5 wt% in another embodiment. In yet another embodiment, from 8 to 0.5 wt% of the monomer mixture is multiolefin.

15 The isoolefin is a C₄ to C₁₂ compound, non-limiting examples of which are compounds such as isobutylene, isobutene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 1-butene, 2-butene, methyl vinyl ether, indene, vinyltrimethylsilane, hexene, and 4-methyl-1-pentene. The multiolefin is a C₄ to C₁₄ multiolefin such as isoprene, butadiene, 2,3-dimethyl-1,3-butadiene, myrcene,
20 6,6-dimethyl-fulvene, hexadiene, cyclopentadiene, styrene, dichlorostyrene and piperylene, and other monomers such as disclosed in EP 0 279 456 and US 5,506,316 and 5,162,425. One embodiment of the butyl rubber polymer of the invention is obtained by reacting 95 to 99.5 wt% of isobutylene with 0.5 to 8 wt% isoprene, or from 0.5 wt% to 5.0 wt% isoprene in yet another embodiment.
25 Butyl-type rubbers and methods of their production are described in detail in, for example, US 2,356,128, 3,968,076, 4,474,924, 4,068,051 and 5,532,312.

 Halogenated butyl rubber is produced by the halogenation of the butyl rubber product described above. Halogenation can be carried out by any means,
30 and the invention is not herein limited by the halogenation process. Methods of halogenating polymers such as butyl polymers are disclosed in US 2,631,984, 3,099,644, 4,554,326, 4,681,921, 4,650,831, 4,384,072, 4,513,116 and 5,681,901.

In one embodiment, the butyl rubber is halogenated in hexane diluent at from 40 to 60°C using bromine (Br₂) or chlorine (Cl₂) as the halogenation agent. The halogenated butyl rubber has a Mooney Viscosity of from 20 to 70 (ML 1+8 at 125°C) in one embodiment, and from 25 to 55 in another embodiment. The halogen wt% is from 0.1 to 10 wt% based in on the weight of the halogenated butyl rubber in one embodiment, and from 0.5 to 5 wt% in another embodiment. In yet another embodiment, the halogen wt% of the halogenated butyl rubber is from 1 to 2.2 wt%.

A commercial embodiment of the halogenated butyl rubber useful in the present invention is Bromobutyl 2222 (ExxonMobil Chemical Company, Houston TX). Its Mooney Viscosity is from 27 to 37 (ML 1+8 at 125°C, ASTM 1646, modified), and the bromine content is from 1.8 to 2.2 wt% relative to the Bromobutyl 2222. Further, cure characteristics of Bromobutyl 2222 are as follows: MH is from 28 to 40 dN·m, ML is from 7 to 18 dN·m (ASTM D2084, modified). Another commercial embodiment of the halogenated butyl rubber is Bromobutyl 2255 (ExxonMobil Chemical Company). Its Mooney Viscosity is from 41 to 51 (ML 1+8 at 125°C, ASTM 1646, modified), and the bromine content is from 1.8 to 2.2 wt%. Further, cure characteristics of Bromobutyl 2255 are as follows: MH is from 34 to 48 dN·m, ML is from 11 to 21 dN·m (ASTM D2084, modified). The invention is not limited to the commercial source of any of the halogenated rubber components.

The halogenated butyl rubber useful in the present invention includes, but is not limited to, brominated butyl rubber, chlorinated butyl rubber, star-branched polyisobutylene rubber, star-branched brominated butyl (polyisobutylene/isoprene copolymer) rubber; isobutylene-bromomethylstyrene copolymers such as isobutylene/meta-bromomethylstyrene, isobutylene/4-bromomethylstyrene, isobutylene/chloromethylstyrene, halogenated isobutylene cyclopentadiene, and isobutylene/4-chloromethylstyrene, and the like halomethylated aromatic interpolymers as in US 4,074,035 and US 4,395,506; isoprene and halogenated isobutylene copolymers, polychloroprene, and the like, and mixtures of any of the

above. Some other exemplary embodiments of the halogenated rubber component are also described in US 5,162,425, 4,703,091, and 4,632,963.

Another embodiment of the unsaturated elastomer useful in the invention is a halogenated or unhalogenated "star-branched" butyl rubber. In one embodiment, the star-branched halogenated butyl rubber ("SBHR") is a composition of a butyl rubber, either halogenated or not, and a polydiene or block copolymer, either halogenated or not. Star-branched butyl rubber and the halogenation process is described in detail in US 4,074,035, 5,071,913, 5,286,804, 5,182,333 and 6,228,978. The invention is not limited by the method of forming the SBHR. The polydienes/block copolymer, or branching agents are typically cationically reactive and are present during the polymerization of the butyl or halogenated butyl rubber, or can be blended with the butyl or halogenated butyl rubber to form the SBHR. The branching agent or polydiene can be any suitable branching agent, and the invention is not limited to the type of polydiene used to make the SBHR. Branching agents include styrene, polybutadiene, polyisoprene, polypiperylene, natural rubber, styrene-butadiene rubber, ethylene-propylene diene rubber, styrene-butadiene-styrene and styrene-isoprene-styrene block copolymers. These polydienes are present, based on the monomer wt%, greater than 0.3 wt% in one embodiment, and from 0.3 to 3 wt% in another embodiment, and from 0.4 to 2.7 wt% in yet another embodiment.

A commercial embodiment of the SBHR of the present invention is Bromobutyl 6222 (ExxonMobil Chemical Company, Houston TX), having a Mooney Viscosity (ML 1+8 at 125°C, ASTM 1646, modified) of from 27 to 37, and a bromine content of from 2.2 to 2.6 wt% relative to the SBHR. Further, cure characteristics of Bromobutyl 6222 are as follows: MH is from 24 to 38 dN·m, ML is from 6 to 16 dN·m (ASTM D2084, modified).

The elastomeric composition may include a blend of at least one or more elastomers described above, and an inducer. Thus, a blend of elastomers may be desirable depending upon the end use application, such as in tire treads, tire

innerliners or innertubes or tire sidewalls. In this regard, useful elastomer blends are blends of brominated poly(isobutylene-co-4-alkylstyrene) elastomer with either polybutadiene, or natural rubber for such tire components as treads and sidewalls, while halogenated butyl rubber or halogenated star-branched butyl rubber, alone or in an elastomer blend, may be useful as an innerliner or innertube component. Examples of such blends that are useful in the present invention are disclosed in US 6,262,178, 6,255,397 B1, 6,242,522, 6,127,472, 5,532,312, 5,333,662, 5,040,583 and 4,607,074.

In any embodiment of the elastomeric composition, an individual elastomer or blend of elastomers may be present in a composition with other components such as the inducer and cure agents, tackifiers, fillers, and other components as described further below. The composition of the elastomer or elastomers is such that the elastomer(s) is present from at least 10 phr in one embodiment, and from at least 20 phr in another embodiment, and from at least 30 phr in yet another embodiment, and up to 100 phr in one embodiment, up to 90 phr in another embodiment, and up to 80 phr in yet another embodiment, wherein the preferred embodiment can be any combination of any lower limit with any upper limit. In one embodiment, the elastomer or elastomers are present in the composition from 10 to 100 phr, and from 20 to 90 phr in another embodiment, and from 30 to 80 in yet another embodiment.

Inducer Compound

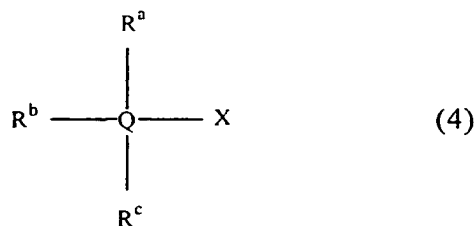
The inducer compound (or "inducer") is a compound that comprises a dissociatable or substitution-labile halogen that is active in, for example, a substitution or elimination reaction. In one embodiment, the inducer compound is contacted with an electrophilic agent such as a zinc or tin compound typically used to cure halogenated rubbers.

In another embodiment, the inducer is any compound possessing a tertiary, allylic or benzylic organohalogen functional group, the halogen preferably being chlorine or bromine, wherein the halogen is capable of dissociating as by, for

example, an elimination reaction or nucleophilic substitution reaction with another compound. Non-limiting examples of these are such compounds as 3-bromopropene, benzyl bromide, triphenylmethylbromide or trimethylbromide and others as described herein. This description is by no means intended to limit the inducer compound to a specific mode of reaction with other compounds, but is presented as representative of embodiments of the invention.

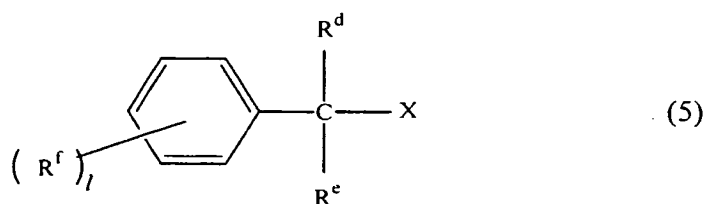
More particularly, the inducer compound is a compound capable of transferring a halogen species to a secondary agent. By "halogen species", it is meant any species such as a halogen anion or radical. Examples of halogen species are chlorine anion (Cl^-), bromine anion (Br^-), chlorine radical (Cl^\cdot) or bromine radical (Br^\cdot), such as is known in the art and described in, for example, *Morrison and Boyd*, ORGANIC CHEMISTRY 46-49 (Allyn and Bacon, Inc. 5th ed., 1987). By "capable of transferring", it is meant that the halogen species can react by, for example, nucleophilic substitution reactions with a secondary agent, or by dissociation into a medium such as an organic solvent or elastomeric phase, followed by reaction with the secondary agent, or, alternatively, by any substitution-type reaction as is commonly known. The transfer may be partial or complete, meaning that only a certain percentage of the dissociable or substitution-labile halogen species may be transferred. By "secondary agent", it is meant any electrophilic moiety or compound such as, for example, the elastomer or a functional group on the elastomer, or a cure agent or a functional group on a cure agent. The terms above have their usual and ordinary meaning such as defined in, for example, *Morrison and Boyd*, ORGANIC CHEMISTRY 174-218 (Allyn and Bacon, Inc. 5th ed., 1987) and HAWLEY'S CONDENSED CHEMICAL DICTIONARY 809, 1056 (13th ed. 1997). Thus, the inducer may transfer, for example, a bromine anion or radical to a zinc ethylhexanoate cure agent, or to a unsaturated elastomer, or to some other metal oxide or metal carboxylate in one embodiment of the invention.

In a particular embodiment, the inducer can be described as having the structure (4):



wherein Q is selected from carbon, silicon, and germanium, X is a halogen, and
 R^a, R^b and R^c are the same or different and are selected from hydrogen, a C₁ to C₂₆
 5 alkyl in one embodiment, a C₁ to C₁₀ alkyl in another embodiment; a C₁ to C₂₆
 substituted alkyl, aryl, or substituted aryl in another embodiment, a C₁ to C₁₂
 substituted alkyl, aryl, or substituted aryl in another embodiment, these terms
 having the same meaning as described above. In one embodiment, Q is carbon,
 and X is chlorine, bromine, or iodine, and at least one of R^a, R^b and R^c are
 10 substituted aryl groups. Adjoining R^a, R^b and R^c groups may form a fused ring or
 aromatic ring system.

In another embodiment, the inducer can be described by the following
 structure (5):



wherein *l* can have a value of from 1 to 5 in one embodiment, and from 1 to 2 in
 an alternate embodiment; and wherein X is a halogen, R^d and R^e are the same or
 different and are selected from a hydrogen, a C₁ to C₂₆ straight, branched chain,
 20 and substituted alkyl, and a phenyl or substituted phenyl group, and a C₁ to C₁₂
 straight, branched chain, and substituted alkyl, and a phenyl or substituted phenyl
 group in another embodiment; and R^f is selected from hydrogen, a C₁-C₁₀ alkyl
 group, a C₁-C₃ alkyl group in another embodiment, a C₁-C₁₀ alkoxy group, a C₁-

C₃ alkoxy group in another embodiment, a C₆-C₁₀ aryl group, a C₆-C₈ aryl group in another embodiment, a C₆-C₁₀ aryloxy group, a C₆-C₈ aryloxy group in another embodiment, a C₂-C₁₀ alkenyl group, a C₂-C₄ alkenyl group in another embodiment, a C₇-C₄₀ arylalkyl group, a C₇-C₁₀ arylalkyl group in another embodiment, a C₇-C₄₀ alkylaryl group, a C₇-C₁₂ alkylaryl group in another embodiment, a C₈-C₄₀ arylalkenyl group, a C₈-C₁₂ arylalkenyl group in another embodiment, and a halogen atom; and wherein adjoining aryl structures may form a fused aryl structure.

10 In yet another embodiment of structure (5), the inducer compound is a mono-, di- or tri- (substituted) aryl methyl halide, such that, for example, R^d and R^e in (5) are the same or different and are substituted phenyl or naphthyl groups or hydrogen, and the halide is a bromide or chloride.

15 In yet another embodiment of structure (5), X is a bromine, and R^d and R^e are the same or different and are either hydrogen or methyl groups, and R^f is as described above. In another embodiment of structure (5), at least one of R^d or R^e are substituted aryl groups. Non-limiting examples of the inducer compound of structures (4) and (5) include benzyl bromide (α -bromotoluene), α -chlorotoluene, 20 1-bromonaphthalene, 1-chloronaphthalene, 4-bromobenzoic acid, 4-chlorobenzoic acid, methyl α -bromophenylacetate, methyl α -chlorophenylacetate, triphenylmethylbromide (bromotriphenylmethane), chlorotriphenylmethane, diphenylmethylbromide, diphenylmethylchloride, (3-bromopropyl)benzene, 4-bromomethylbenzophenone, brominated vegetable oil, chlorinated vegetable oil, 25 2-ethylhexylbromide, 2-ethylhexylchloride, bromomethyl phenyl sulfone, 4-(bromomethyl)phenylacetic acid, 4-methylbenzylbromide, 2-bromo-2-methylpropane, 2-chloro-2-methylpropane, 4-methylbenzylchloride, 2-methylbenzylbromide, 2-methylbenzylchloride, 1-bromo-3-(bromomethyl)adamantane, 1-bromoadamantane, bromobornane, chlorobornane, 30 9-bromophenanthrene, bromophenol blue (3',3'',5',5''-tetrabromophenolsulfonephthalein sodium salt), 9-bromofluorene, 4-bromophenol, 4-(trifluoromethyl)benzyl bromide, α^2 -chloroisodurene, 2-

(chloromethyl)anthraquinone, and 2,4-bis(trifluoromethyl)benzyl bromide, and mixtures thereof.

In yet embodiment, the inducer compound may be a relatively low molecular weight polymer. For example, in one embodiment, inducer is a halogenated tackifier resin, such as a halogenated ESCOREZ™ Resin (ExxonMobil Chemical Co., Houston TX.). These resins are aliphatic resins with a weight average molecular weight (MW) in the range of 2000 to 5000, and a number average molecular weight (MN) of from 600 to 900. In yet another embodiment, the inducer is a BIMS polymer having a molecular weight in the range of from 2000 to 5000 in one embodiment, and from 1500 to 6000 in another embodiment, and a level of bromination of from 0.05 to 2 mol% relative to the BIMS polymer in one embodiment, and from 0.1 to 0.9 mol% in another embodiment.

In any case, the inducer compound or blend of inducer compounds as described in any embodiment above becomes part of the elastomer composition of the invention. In one embodiment, the inducer compound(s) is present from at least 0.1 phr in one embodiment, and from at least 0.5 phr in another embodiment, and from at least 0.8 phr in yet another embodiment, and up to 20 phr in one embodiment, up to 10 phr in another embodiment, and up to 8 phr in yet another embodiment, wherein the preferred embodiment can be any combination of any lower limit with any upper limit. Alternatively, the inducer is present from 0.1 to 20 phr, or from 0.5 to 10 phr in another embodiment, or from 0.8 to 8 phr in yet another embodiment.

Cure Agent

Generally, elastomeric compositions, e.g., those used to produce tires, are crosslinked using at least one of any number of cure agents. It is known that the physical properties, performance characteristics, and durability of vulcanized rubber compounds are directly related to the number (crosslink density) and type of crosslinks formed during the vulcanization reaction. See, e.g., Helt et al., *The Post*

Vulcanization Stabilization for NR, RUBBER WORLD 18-23 (1991). Generally, elastomer blends may be crosslinked by adding curative molecules, for example sulfur, metal oxides (i.e., zinc oxide), metal carboxylates, organometallic compounds, radical inducers, etc. followed by heating or other radiative treatment.

5 Cure systems for halogenated butyl rubber are described in RUBBER TECHNOLOGY 312-316 (Maurice Mortin, ed., Chapman & Hall 1995), and in US 5,373,062.

The cure agent of the present invention may include any number of components such as a metal or metal ligand complex, accelerators, resins or other

10 components known in the art to cause a cure of an elastomer. In one embodiment, the cure agent is at least a Group 2-14 metal oxide or metal ligand complex, wherein at least one ligand is able to undergo a substitution reaction with the inducer compound. In one embodiment, the at least one cure agent is a metal oxide which includes zinc oxide, hydrated lime, magnesium oxide, alkali

15 carbonates, and hydroxides. In particular, the following metal-based cure agents are common curatives that will function in the present invention: ZnO, CaO, MgO, Al₂O₃, CrO₃, FeO, Fe₂O₃, and NiO, and/or carboxylates of these metals. These metal oxides can be used in conjunction with the corresponding metal carboxylate complex, or with the carboxylate ligand, and either a sulfur compound or an

20 alkylperoxide compound. (See also, *Formulation Design and Curing Characteristics of NBR Mixes for Seals*, RUBBER WORLD 25-30 (1993).

These metal oxides can be used in combination with another compound such as a fatty acid, and the cure agent is not herein limited to the metal oxide or

25 metal ligand complex alone. Examples of organic or fatty acids that can be used in the invention are stearic, oleic, lauric, palmitic, myristic acids, and mixtures thereof, and hydrogenated oils from palm, castor, fish, and linseed oils. The use of these cure agents is discussed in RUBBER TECHNOLOGY 20-58 (Maurice Mortin, ed., Chapman & Hall 1995), and in *Rubber World Magazine's BLUE BOOK 2001*

30 109-137 (Don R. Smith, ed., Lippincott & Peto, Inc. 2001); and US 5,332,787.

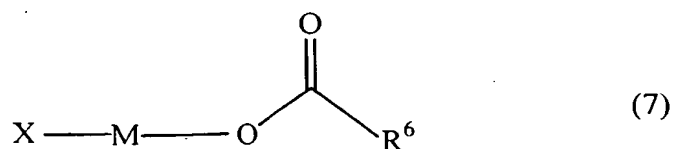
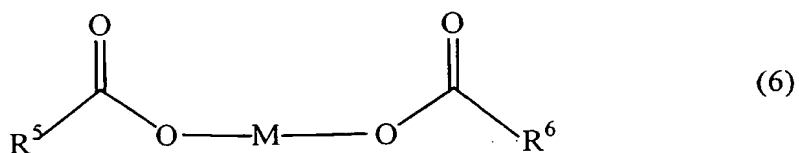
The use of zinc oxide and carboxylates and carboxylic acids, or zinc carboxylates and other metal ligand complexes as a cure catalyst for such elastomers as brominated poly(isobutylene-co-4-methylstyrene) is known in the art, such as disclosed by *Frechet et al.*, 66 RUBBER CHEMISTRY AND TECHNOLOGY 98-108 (1992) and *Bielski et al.*, 31 JOURNAL OF POLYMER SCIENCE: PART A: POLYMER CHEMISTRY 755-762 (1993), and in US 5,656,694; and for halobutyl-type rubbers in RUBBER TECHNOLOGY 312-316 (Maurice Morton, ed., Chapman & Hall 1995), and in US 5,373,062 and US 4,227,915.

In one embodiment, in conjunction with the use of the metal-based cure agent, a phenolic resin is also employed to cure BIMS and other elastomers. In particular, it is desirable to use a halogenated phenolic resin to cure compositions of BIMS when no inducer is present. One such resin is a bromomethyl and hydroxymethyl-based alkyl phenol-formaldehyde resin sold commercially as SP 1045 (non-brominated) and SP-1055 (brominated). See, for example, *Leghaus et al.*, 41 POLYMER 1973-1979 (2000) and *Duvdevani et al.*, RUBBER WORLD 28 (August 1997). These resins may be present in the composition from 0.1 to 30 phr in one embodiment, and from 0.5 to 20 phr in another embodiment, and from 1 to 10 phr in yet another embodiment. When the inducer compound is present as a cure additive, a non-halogenated phenolic resin can be used. By non-halogenated, it is meant that the alkyl-functional group present on the resin may include such moieties as hydroxyl or alkoxy, but excludes halogen. The term "non-halogenated" in reference to the phenolic resin here does not exclude the possibility that there may be a halogen directly on the aromatic ring. In one embodiment of the invention, an inducer compound is used in conjunction with a non-halogenated phenolic resin and a metal oxide or other metal ligand complex. The use of a non-halogenated (no halogen on the alkyl group pendant from the phenolic ring) resin is preferable when curing unsaturated elastomers by the method of the invention.

In a desirable embodiment, halogenated phenolic resins such as, for example, SP1055 and SP1056 (Schenectady International), are substantially

absent, meaning that they are present, if at all, to an extent no greater than 1 phr of the composition in one embodiment, and less than 0.5 phr in another embodiment, and less than 0.1 phr in yet another embodiment, and not added at all (0 phr) in yet another embodiment. In yet another embodiment, a halogenated phenolic resin is present with the inducer, the halogenated resin present from 0.5 phr to 10 phr of the composition to be cured.

In yet another embodiment, the cure agent is any compound that, when contacted with the structure (6), will result in a structure (7):



wherein M is a Group 3-14 metal, preferably tin or zinc, and R⁵ and R⁶ are the same or different and are defined as R^a and R^c. More specifically, in one embodiment of structure (7), X is a halogen, M is a Group 3-14 metal, and R⁶ is selected from a hydrogen and a C₁ to C₂₆ straight or branched chain alkyl, a substituted alkyl, and a substituted aryl. In an embodiment of the method of curing a substituted phenylic elastomer of the invention, a cure agent such as zinc 2-(ethylhexanoate), which corresponds to structure (6), can be contacted with the inducer compound to form the structure corresponding to (7). Thus, the cure agent and inducer are contacted *in situ* with the substituted phenylic elastomer in one embodiment to cause a cure. The compound represented in structure (6) may constitute the cure agent.

In yet another embodiment of the invention, the cure agent is described by structure (7) above. This structure can be formed by any means, *in situ* or otherwise, and is not limited by the method of producing the compound. In one embodiment of structure (7), X is a halogen, preferably chlorine or bromine, and -OOR⁶ is a carboxylate wherein R⁶ is as described above, examples of which are stearic, oleic, lauric, palmitic, and myristic acids, and mixtures thereof, and hydrogenated oils from palm, castor, fish, and linseed oil acids; and M is Group 3-14 metal, preferably zinc or tin. In the embodiment where the cure agent can be described by structure (7), the inducer may or may not be present. Thus, one embodiment of the invention includes a method of curing an elastomer which consists essentially of contacting the structure (7) and the elastomer.

As part of the composition of the invention, the cure agent may be present from 0.1 to 10 phr in one embodiment, from 0.5 to 8 phr in another embodiment, and from 1 to 5 phr in yet another embodiment.

Acceleration of the cure process may be accomplished by adding to the blend an amount of an accelerant, often an organic compound. The mechanism for accelerated vulcanization of natural rubber involves complex interactions between the curative, accelerator, activators and polymers. Ideally, all of the available curative is consumed in the formation of effective crosslinks which join together two polymer chains and enhance the overall strength of the polymer matrix. Numerous accelerators are known in the art and include, but are not limited to, the following: stearic acid, diphenyl guanidine (DPG), tetramethylthiuram disulfide (TMTD), 4,4'-dithiodimorpholine (DTDM), tetrabutylthiuram disulfide (TBTD), 2,2'-benzothiazyl disulfide (MBTS), hexamethylene-1,6-bisthiosulfate disodium salt dihydrate, 2-(morpholinothio) benzothiazole (MBS or MOR), blends of 90% MOR and 10% MBTS (MOR 90), N-tertiarybutyl-2-benzothiazole sulfenamide (TBBS), and N-oxydiethylene thiocarbamyl-N-oxydiethylene sulfonamide (OTOS) zinc 2-ethyl hexanoate (ZEH), N, N'-diethyl thiourea.

Additional Components: Additives, Rubbers & Fillers

The compositions produced in accordance with the present invention may also contain other components and additives customarily used in elastomeric blends. In one embodiment, a tackifier such as an aliphatic hydrocarbon resin may be added
5 from 0.1 to 10 phr. Such compounds are sold commercially under the trade name ESCOREZ™ (ExxonMobil Chemical Co., Houston TX). Other components include compounds such as effective amounts of processing oils, pigments, accelerators, other crosslinking and curing materials, antioxidants, antiozonants, fillers and naphthenic, aromatic or paraffinic extender oils if the presence of an extension oil is
10 desired. Accelerators include amines, guanidines, thioureas, thiazoles, thiurams, sulfenamides, sulfenimides, thiocarbamates, xanthates, and the like. Peroxide cure systems may also be used.

The composition of the invention may also include one or a mixture of other
15 additional components such as elastomers, thermoplastics or polymers that may or may not be curable. Non-limiting examples of such rubbers include natural rubber, butyl rubber, polybutadiene, polyisoprene, poly(styrene-*co*-butadiene), poly(styrene-isoprene-butadiene); poly(isobutylene-*co*-4-alkylstyrene), halogenated poly(isobutylene-*co*-4-methylstyrene), halogenated butyl rubber, star-
20 branched butyl rubber, halogenated star-branched butyl rubber, polyethylene, polypropylene, polypropylene copolymers and impact copolymers, ethylene-propylene rubber, polysulfide, polycarbonate, nitrile rubber, propylene oxide polymer, acrylates and acetates, star-branched butyl rubber, nylons, thermoplastic resins, other saturated polymers such as polyisobutylene and other elastomers and
25 polymers disclosed herein.

In one embodiment, the additional elastomer is a saturated polymer. By saturated polymer, it is meant to include those polymers which have saturated backbone but may have pendant unsaturation. Illustrative of such polymers are low,
30 medium or high density polyethylene or copolymers of ethylene with up to about 50 wt% of a C₃ to C₈ monoolefin such as propylene, isobutylene, 1-butene, 1-hexene and the like. Preferred ethylene polymers are polyethylene and elastomeric

copolymers of ethylene containing up to about 35 wt% of polymerized propylene. Optionally the blend may additionally contain an EPDM such as elastomeric copolymers of ethylene, propylene and a non-multiolefin such as ethylidene-norbornene. Particularly preferred ethylene copolymers are plastomers polymerized using metallocene polymerization catalyst, such as copolymers of ethylene with from about 5 to 30 wt% of 1-hexene or 1-butene, such as available under the EXACT™ tradename from ExxonMobil Chemical Co, Houston TX. Suitable ethylene polymers useful as blend components generally exhibit a Melt Index in the range of from about 0.5 to 600, more preferably from about 1 to 25.

In another embodiment, the additional rubber component may be a rubber such as natural rubber and polybutadiene rubbers. Natural rubbers are described in detail by *Subramaniam* in RUBBER TECHNOLOGY 179-208 (Maurice Morton, ed., Chapman & Hall 1995). Desirable embodiments of the natural rubbers of the present invention are selected from the group consisting of Malaysian rubber such as SMR CV, SMR 5, SMR 10, SMR 20, and SMR 50 and mixtures thereof, wherein the natural rubbers have a Mooney viscosity at 100°C (ML 1+4) of from 30 to 120, more preferably from 40 to 65. The Mooney viscosity test referred to herein is in accordance with ASTM D-1646.

Some commercial examples of rubbers useful in the present invention are NATSYN™ (Goodyear Chemical Company), and BUDENE™ 1207 or BR 1207 (Goodyear Chemical Company). A desirable covulcanate is high cis-polybutadiene (cis-BR). By "cis-polybutadiene" or "high cis-polybutadiene", it is meant that 1,4-cis polybutadiene is used, wherein the amount of cis component is at least 95%. An example of high cis-polybutadiene commercial products used in the covulcanized composition BUDENE™ 1207.

The additional elastomer may be present in the composition in a range from 20 to 95 phr in one embodiment, from 30 to 80 phr in another embodiment, and from 40 to 70 in yet another embodiment.

The composition of the invention may have one or more filler components such as calcium carbonate, clay, mica, silica and silicates, talc, titanium dioxide, and carbon black. The filler may be present up to 150 phr in one embodiment, and up to 100 phr in another embodiment, and present in at least 10 phr in one
5 embodiment, and present in at least 20 phr in another embodiment.

In one embodiment, the filler is carbon black or modified carbon black. The preferred filler is semi-reinforcing grade carbon black present at a level of from 10 to 150 phr of the blend, more preferably from 30 to 120 phr. Useful
10 grades of carbon black as described in RUBBER TECHNOLOGY 59-85 (Maurice Morton, ed., Chapman & Hall 1995) range from N110 to N990. More desirably, embodiments of the carbon black useful in, for example, tire treads are N229, N351, N339, N220, N234 and N110 provided in ASTM (D3037, D1510, and D3765). Embodiments of the carbon black useful in, for example, sidewalls in
15 tires, are N330, N351, N550, N650, N660, and N762. Embodiments of the carbon black useful in, for example, innerliners for tires are N550, N650, N660, N762, and N990.

The present invention includes compositions of one or more elastomers with the inducer compound. For example, in one curable composition, a BIMS
20 compound may be present from 10 to 90 phr with the inducer compound present from 0.1 to 20 phr. Another rubber component such as natural rubber or cis-polybutadiene rubber may also be present from 40 to 70 phr in one embodiment. A cure agent is typically present and may include a metal oxide or metal ligand
25 complex present from 0.1 to 10 phr, and a non-halogenated phenolic resin present from 0.1 to 30 phr. In one embodiment, the composition includes a filler such as carbon black from 30 to 120 phr.

In one embodiment of the invention, the composition consists essentially
30 of a halogenated elastomer, a metal oxide or metal ligand complex as the cure agent, an inducer, a filler, and another rubber component. In another embodiment, the composition will consists essentially of the substituted phenylic elastomer, the

inducer, another rubber component, a cure agent such as a metal ligand complex, and carbon black filler.

5 In another embodiment of the invention, the composition includes a halogenated elastomer and an inducer, wherein the halogenated elastomer is selected from brominated poly(isobutylene-co-4-alkylstyrene) elastomer comprising 4-alkylstyrene units and 4(bromoalkyl)styrene units, halogenated butyl rubber, and halogenated star-branched butyl rubber, and mixtures thereof. The halogenated elastomer is present from at least 10 phr in one embodiment, and 10 from at least 20 phr in another embodiment, and from at least 30 phr in yet another embodiment, and up to 100 phr in one embodiment, up to 90 phr in another embodiment, and up to 80 phr in yet another embodiment, wherein the preferred embodiment can be any combination of any lower limit with any upper limit. In one embodiment, the halogenated elastomer is present in a composition 15 from 10 to 100 phr, and from 20 to 90 phr in another embodiment, and from 30 to 80 in yet another embodiment. These components may be blended by any suitable means common in the art.

Methods of Blending Components

20 The methods and compositions disclosed herein are suitable for use in any number of articles of manufacture. Particularly desirable articles are tire components, hoses, belts, sealing rings and damping structures as disclosed in, for example, THE VANDERBILT RUBBER HANDBOOK 596-772 (R.T. Vanderbilt Company, Inc. 1990). In particular, the present invention is useful in the 25 manufacture of tires and tire components such as tire treads, sidewalls and innerliners. Methods of manufacturing tires and tire components are disclosed in, for example, *F.J. Kovac's TIRE TECHNOLOGY* 75-89 (Goodyear Tire and Rubber Company 1978) and in US 6,241,501 and 4,176,702. Examples of tire component formulations and general methods of manufacture are discussed by *Waddell et al.* 30 in THE VANDERBILT RUBBER HANDBOOK 596-621 (R.T. Vanderbilt Company, Inc. 1990). Elastomeric components made from the compositions and methods of the

present invention are not limited to the method of manufacture, as the description is representative only of embodiments of the invention.

5 The components described above are mixed or contacted with one another by conventional means known to those skilled in the art, in a single step or in stages. In one embodiment, the carbon black is added in a different stage from the cure agent and other cure activators and accelerators. In another embodiment, antioxidants, antiozonants and processing materials are added in a stage after the carbon black has been processed with the elastomeric composition, and zinc oxide
10 is added at a final stage to maximize compound modulus. Thus, a two to three (or more) stage processing sequence is preferred. Additional stages may involve incremental additions of filler and processing oils.

15 It is desirable to mix and handle (process) the components in contact with one another at a temperature that avoids curing of the composition. Processing of the composition may take place from 10°C to 140°C in one embodiment, and from 25°C to 135°C in another embodiment. In yet another embodiment, the processing of the composition takes place at a maximum of 140°C. The inducer may be added at any stage of the mixing process prior to curing.

20 Advantageously, the composition of the present invention can be cured at desirably low temperatures. The compositions may be cured by subjecting them using heat or radiation according to any conventional cure process, or by applying only minimal heating. Curing may be conducted at a temperature ranging from
25 greater than from 25°C in one embodiment, and at greater than from 85°C in another embodiment, and at greater than from 100°C in yet another embodiment. Alternately, the curing can take place from 25°C to 250°C in one embodiment, from 85°C to 200°C in another embodiment, and from 100°C to 180°C in yet another embodiment for any length of time, such as, for example from 1 to 150
30 minutes.

Suitable elastomeric compositions for such articles as tire components may be prepared by using conventional mixing techniques including, e.g., kneading, roller milling, extruder mixing, internal mixing (such as with a Banbury™ mixer) etc. The sequence of mixing and temperatures employed are well known to skilled rubber compounders, the objective being the dispersion of fillers, activators and curatives in the polymer matrix without excessive heat buildup. A useful mixing procedure utilizes a Banbury™ mixer in which the elastomer, carbon black, inducer compound and cure agents are added and the composition is mixed for the desired time or to a particular temperature to achieve adequate dispersion of the ingredients. Alternatively, the rubber and a portion of the carbon black (e.g., one-third to two thirds) is mixed for a short time (e.g., about 1 to 3 minutes) followed by the remainder of the carbon black and other components. Mixing is continued for about 5 to 10 minutes at high rotor speed during which time the mixed components reach a temperature of about 140°C. Following cooling, the components are mixed in a second step on a rubber mill or in a Banbury™ mixer during which the curing agent and optional accelerators, are thoroughly and uniformly dispersed at relatively low temperature, e.g., from 80°C to 105°C in one embodiment, to avoid premature curing of the composition. Variations in mixing will be readily apparent to those skilled in the art and the present invention is not limited to any specific mixing procedure. The mixing is performed to disperse all components of the composition thoroughly and uniformly.

As an example of one article that can be produced from the composition of the invention, an innerliner stock can then be prepared by calendering the compounded rubber composition into sheet material having a thickness of roughly 40 to 80 mil gauge and cutting the sheet material into strips of appropriate width and length for innerliner applications. Stock for sidewall, treads, hoses, and other articles can also be prepared by methods known in the art.

The sheet stock at this stage of the manufacturing process is a sticky, uncured mass and is therefore subject to deformation and tearing as a consequence of handling and cutting operations associated with tire construction.

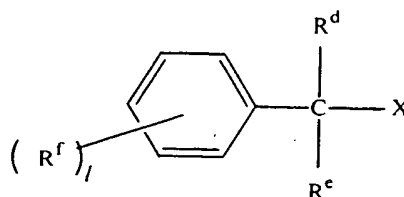
5 The innerliner, for example, is then ready for use as an element in the construction of a pneumatic tire. The pneumatic tire is composed of a layered laminate comprising an outer surface which includes the tread and sidewall elements, an intermediate carcass layer which comprises a number of plies containing tire reinforcing fibers, (e.g., rayon, polyester, nylon or metal fibers)
10 embedded in a rubbery matrix and an innerliner layer which is laminated to the inner surface of the carcass layer. Tires are normally built on a tire forming drum using the layers described above. After the uncured tire has been built on the drum, the uncured tire is placed in a heated mold having an inflatable tire shaping bladder to shape it and heat it to one of many cure temperatures by methods well
15 known in the art. Cure temperatures generally range from 25°C to 250°C, more preferably from 85°C to 200°C, and times may range from about one minute to several hours, more preferably from about 5 to 30 minutes. Curing of the assembled tire results in curing of all elements of the tire assembly, i.e., the innerliner, the carcass and the outer tread/sidewall layers and enhances the
20 adhesion between these elements, resulting in a cured, unitary tire from the multi-layers.

 The composition of the present invention may be used in producing innerliners, treads, and sidewalls for motor vehicle tires such as truck tires, bus
25 tires, passenger automobile tires, motorcycle tires, off the road tires, and the like. The composition may also be used to make hoses, belts, damping devices, and other articles where damping, flexibility, and abrasion resistance is a desirable feature.

30 One embodiment of the invention is a method of forming a component in an vehicle tire and/or air barrier comprising contacting at least one uncured elastomer; at least one cure agent; and an inducer compound containing a

dissociable or substitution labile halogen capable of transfer to the elastomer and/or the cure agent during curing; thus forming a blend; and maintaining the blend under conditions to effect the desired level of curing. The components are contacted at a temperature of from 25°C to 250°C to form a cured elastomeric composition in one embodiment, and from 25°C to the melting point of the elastomer to form a cured elastomeric composition in another embodiment.

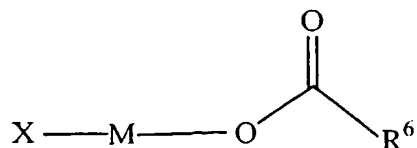
In one embodiment, the inducer compound possesses a tertiary, allylic or benzylic organohalogen functional group capable of transferring a halogen atom. In another embodiment, the inducer is represented by the following formula:



wherein l is from 1 to 5, X is a halogen, R^d and R^e are the same or different, and are selected from hydrogen, a C_1 to C_{26} straight, branched chain, and substituted alkyl, and a phenyl or substituted phenyl; and R^f is selected from the group consisting of a hydrogen atom, a C_1 - C_{10} alkyl group, a C_1 - C_{10} alkoxy group, a C_6 - C_{10} aryl group, a C_6 - C_{10} aryloxy group, a C_2 - C_{10} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_7 - C_{40} alkylaryl group, a C_8 - C_{40} arylalkenyl group, and a halogen atom.

The inducer may be selected from a benzyl bromide (α -bromotoluene), 1-bromonaphthalene, 4-bromobenzoic acid, methyl α -bromophenylacetate, triphenylmethylbromide (bromotriphenylmethane), 4-bromomethylbenzophenone, brominated vegetable oil, 2-ethylhexylbromide, bromomethyl phenyl sulfone, 4-(bromomethyl)phenylacetic acid, 4-(trifluoromethyl)benzyl bromide, α^2 -chloroisodurene, 2-(chloromethyl)anthraquinone, 2,4-bis(trifluoromethyl)benzyl bromide, and mixtures thereof in yet another embodiment.

Further, the cure agent may be described by the following structure:



wherein X is a halogen, M is a Group 3-14 metal, and R⁶ is selected from a hydrogen and a C₁ to C₂₆ straight or branched chain alkyl, a substituted alkyl, and a substituted aryl.

In one embodiment, the inducer is present from 0.1 to 20 phr in the components contacted with one another.

In yet another embodiment, the elastomer is selected from an unsaturated elastomer and a substituted phenylic elastomer. The elastomer may be selected from butyl rubber, natural rubber, polyisoprene, polybutadiene, poly(isobutylene-*co*-4-alkylstyrene), brominated poly(isobutylene-*co*-4-alkylstyrene), halogenated butyl rubber, and halogenated star-branched butyl rubber, poly(styrene-*co*-butadiene), polysulfide, nitrile rubber, propylene oxide polymers and mixtures thereof in yet another embodiment, and is desirably a brominated poly(isobutylene-*co*-4-alkylstyrene), wherein the 4-alkylstyrene is 4-methylstyrene present in the copolymer from 4 wt% to 15 wt% of the copolymer in one embodiment, and from 0.20 mol% to 3.0 mol% of the brominated poly(isobutylene-*co*-4-alkylstyrene) comprises 4-bromomethylstyrene in another embodiment.

In yet another embodiment, the at least one cure agent is a metal oxide or a metal ligand complex, or mixtures thereof. The at least one cure agent may further comprise a non-halogenated phenolic resin in one embodiment, and halogenated phenolic resins may be substantially absent in another embodiment.

In yet a further embodiment, the method includes contacting an additional component selected from natural rubber, butyl rubber, polybutadiene, polyisoprene, poly(styrene-co-butadiene), poly(styrene-isoprene-butadiene); poly(isobutylene-co-4-alkylstyrene), halogenated poly(isobutylene-co-4-methylstyrene), halogenated butyl rubber, star-branched butyl rubber, halogenated star-branched butyl rubber, polyethylene, polypropylene, polypropylene copolymers and impact copolymers, ethylene-propylene rubber, polysulfide, nitrile rubber, polycarbonate, propylene oxide polymer, acrylates and acetates, star-branched butyl rubber, nylons, thermoplastic resins, polyisobutylene and mixtures thereof.

Test Methods

Test methods and the units of measure are outlined in Table 1. Cure and scorch properties were measured according to ASTM D5289-95, using a MDR 2000 at the indicated temperature and 0.5 degree arc, with the following modifications. Properties were measured using an automated MDR with a small non-standard "cruciform" die (Alpha Technologies) made for the automatic MDR, and polyester film (continuous roll about 15 cm inches wide and 0.028 mm thick) as a barrier between the sample and die. Test specimens were cured at the indicated temperature, typically from at 170°C for cure properties, and 135°C for scorch (processing temperature) properties, for a time corresponding to T75 and T90 plus an appropriate mold lag time. Mold lag is the time at the beginning of the test wherein material is still flowing into the grooves of the die and temperature is not yet at the test temperature.

The scorch properties of the compositions were measured at 135°C in order to model the temperature at which typical tire processing occurs, and also at 170°C, a temperature at which the composition cures. The s1 and s3 values, in minutes, represent the time it takes for the viscosity of the composition at 135°C (or any processing temperature) to get to 1 and 3 Mooney units, respectively. The T75 and T90 measure the time, in minutes, it takes the composition to get to 75% and 90% cure state, respectively, relative to their respective final cure states. The

Ts1 and Ts3 values are MDR cure values and measure the time it takes the composition at 170°C (or any cure temperature) to cure to one torque unit from time zero. The measurement of the various parameters at a given temperature is representative to one embodiment of the method of curing the polymer or composition, and is by no means meant to be limiting of the invention.

The values "MH" and "ML" used here and throughout the description refer to "maximum torque" and "minimum torque", respectively. The MH-ML values are a measure of the cure state. The "MS" value is the Mooney scorch value, the "ML(1+4)" value is the Mooney viscosity value. The peak rate is experimentally determined by a rheometer test, and is a measure of the fastest torque increase of the composition, expressed in dNm/min.

EXAMPLES

The present invention, while not meant to be limiting by, may be better understood by reference to the following example and Tables. Table 2 summarizes the various components used in the Examples, and their commercial source. Tables 3-6 summarize the data from Examples A-D. In all tests, a pre-heat of 1 minute elapsed before starting the rotation of the rheometer rotor and acquiring data. A small rotor was used in all cases. Abbreviations for the inducers are listed in the Tables when used in a Figure.

Samples were mixed as follows. The elastomeric components, processing oils, fillers and optionally the phenolic resins were first blended in a Banbury™ mixer for 3 to 8 minutes at from 130°C to 180°C. After blending, the mixture was allowed to cool to room temperature while sheeted on a mill roll. Next, the cure agents to be used and the inducer (when present) were added to a portion cut from the cooled sheet, followed by roll milling for 7 to 20 minutes at from 35°C to 60°C to blend the cure agents and/or inducer into the elastomer blend. This final blend was then tested as described.

Example A--BIMS or polybutadiene without phenolic resin

Table 3A contains the results of Example A masterbatch, which includes 100 phr of EXXPRO™ 3035 (runs 1-3) or 100 phr BUDENE™ 1207 polybutadiene (runs 4-6), each with 60 phr of carbon black N330, and no processing oils. In each, 3
5 phr of Octoate Z cure agent is present, and 3 phr, when present, of the inducer Triphenylmethyl bromide (TPMB) or 4-bromomethylbenzophenone (BMBP). Data for these sample runs are in Table 3A.

These data shown improvement in cure properties for both BIMS elastomer
10 and polybutadiene elastomer in a simple system when certain inducers are part of the composition during curing. The BIMS elastomer shows an improved Ts1 while the T90 value changes only a small amount when BMBP is added. Further, for the BIMS elastomer, s1 shows improvement, while the cure state (MH-ML) changes only a small among for both BMBP and TPMB compositions. Thus, there is an
15 improvement in the independent control of one cure property over another.

For the polybutadiene elastomer, both BMBP and TPMB improve the peak rate and cure state (MH-ML). These data in Example A for a simple system show that the inducers can be used to improve the cure of compositions that include the
20 inducers of the present invention. The examples below serve to illustrate how the addition of other additives and cure agents, typical in elastomer curing, can further enhance the advantages of the methods and compositions of the invention.

In a further blend (not shown in a table) to duplicate a desirable sidewall
25 blend of a BIMS and polybutadiene rubber with a processing oil, the following composition was tested: 35 phr of EXXPRO™ 3035, 65 phr of BUDENE™ 1207, 15 phr of CALSOL™ 810 processing oil, 4.5 phr ESCOREZ™ 1102 tackifying agent, 60 phr of N300 carbon black, and 1.5 phr of SP-1068 (brominated phenolic resin) were blended, followed by addition of 3 phr of Octoate Z cure agent and 3 phr
30 of either BMBP or TPMB. These were tested for scorch safety and cure characteristics. Table 3B shown these data.

The results for the BIMS/polybutadiene blend indicate an improvement in the scorch and cure properties for blends of elastomers when the inducers are present. In particular, the data in Table 3B show the benefits of using TPMB as an inducer compound. The scorch (s10) value is improved for the TPMB relative to no inducer, and the peak rate is improved, while the T90 values are relatively unchanged.

Example B--BIMS and polybutadiene blend

Table 4 contains the results of Example B masterbatch, which includes 65 phr BUDENE™ 1207, 35 phr of EXXPRO™ 3035, 60 phr N330 carbon black, 15 phr of CALSOL™ 810, and 4.5 phr ESCOREZ™ 1102. The Example B master batch is 166 phr. The compositions in Example B are suitable for, for example, tire sidewalls. Various amounts of other components and inducers are as indicated in Table 4. The cure data (170°C) for Example B is listed in Table 4, and shown graphically in Figures 1, 2 and 3. The data is taken as MDR Auto, 170°C, 0.5° Arc, 60 min total cure time.

All sample runs in the Example are using an inducer. The data in Figure 2 shows that the peak rate can be increased without changing the cure state using the BNAP, BBA and MBPA inducers as compared to the SP-1055 cured samples without an inducer compound (see Table 5 for the data for the non-initiated comparative sample run). Further, Figure 3 shows that the scorch s1 (135°C) values can be improved without altering the cure state (MH-ML). The BNAP inducer achieved the greatest increase in s1 (135°C) as compared to the comparative run using SP-1055 phenolic resin. Finally, the data in Figure 1 show that the cure time can be reduced while the scorch time is maintained using the inducers.

Example C--BIMS & polybutadiene blend

Table 5 contains the results of Example C masterbatch, which includes 65 phr BUDENE 1207, 35 phr of EXXPRO™ 3035, 60 phr N330 carbon black, 15 phr of CALSOL™ 810, and 4.5 phr ESCOREZ™ 1102, as in Example B. In run 10, an additional 0.5 phr of SP-1045 (non-halogenated phenolic resin) was added. The

compositions in Example C are suitable for, for example, tire sidewalls. Various amounts of other components and inducers are as indicated in Table 4. The cure data (170°C) for Example C is listed in Table 5, and shown graphically in Figures 4, 5 and 6. The data is taken as MDR Auto, 170°C, 0.5° Arc, 60 min total cure time. The scorch data is all at 135°C.

The runs 1-3 are comparative runs for this Example C and for Example B above, and are without inducers. The data in Figure 5 shown that the inducers, in particular TPMB, advantageously increases the peak rate at a low cure states. Also, the s1 (135°C) values can be improved without altering the MH-ML values (cure state) as indicated in Figure 6. In particular, the BVO and BMBP inducers improve the scorch s1 (135°C) values. Finally, the cure time can be advantageously reduced while the scorch time s1 (135°C) is advantageously increased for the samples with an inducer compound, as shown in Figure 4, wherein the s1 (135°C) values are improved for the runs with BMBP and BVO inducers relative to the non-initiated run.

Example D--BIMS of differing bromine levels and Natural Rubber

Table 6 contains the results of Example D masterbatches, which includes composition of two different types of brominated poly(isobutylene-co-4-methylstyrene). Compositions 1-4 contain the following: 70 phr of EXXPRO™ 96-4, 30 phr of SMR 20 natural rubber, 20 phr of N330 carbon black, and 30 phr of CALSOL™ 810. Compositions 5-8 contain the following: the first pass contained 35 phr of EXXPRO™ 3035, 15 phr of SMR 20 natural rubber, 10 phr of N330 carbon black, 30 phr of Burgess 2211, and 15 phr of CALSOL™ 810; the second pass contained the composition of the first pass in addition to 50 phr SMR 20, 20 phr N330, 1.5 phr SP-1068 resin, and 4.5 phr ESCOREZ™; the third pass contained an additional amount of SP-1045 listed in Table 6. Other components in Compositions 1-8 are listed in Table 6.

These data show that the improvement in s1 (135°C) relative to the cure state (MH-ML) follows a similar pattern in both the 0.48 mol% bromine BIMS

and in the 0.85 mol% bromine BIMS. The s_1 values advantageously increase, as do the peak rates, while maintaining the cure state (MH-ML).

Example E--BIMS and Natural Rubber

5 This example is using a two-pass mixing process. In this example (blends 1-10), a first pass master batch contained the following: 35 phr EXXPRO 3035, 15 phr natural rubber (SMR 20), 10 phr carbon black N330, 30 phr BURGESS™ 2211, and 15 phr CALSOL™ 810. Total phr of the first pass batch was 105 phr. This first batch was then blended in a second pass with 50 phr of natural rubber
10 (SMR 20), 20 phr carbon black N330, 1.5 phr of SP-1068, and 4.5 phr ESCOREZ™. The cure agent and inducers were then added as described above, the cure agent being OCTOATE Z powder at 3 phr in each of blends 1-10.

 The data in Table 7 reflect the advantages of the blend. For example, there
15 is again seen an increase in the scorch when using the inducer compound, and independent control of the scorch relative to the cure as measured by the MH-ML and T90.

 While the present invention has been described and illustrated by
20 reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to many different variations not illustrated herein. For these reasons, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

25 All priority documents are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted. Further, all documents cited herein, including testing procedures, are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted.

TABLE 1. Test Methods

Parameter	Units	Test
Mooney Viscosity (polymer)	ML 1+4, 125°C, MU	ASTM D 1646
Mooney Viscosity (compound)	ML 1+4, 100°C, MU	ASTM D 1646
Mooney Scorch Time, s1, 3, 135°C or 170°C	minutes	ASTM D 1646
Oscillating Disk Rheometer (MDR) @ 170°C, $\pm 0.5^\circ$ arc ML MH T _S 1, 3 T ₇₅ , T ₉₀ Cure rate, peak rate	dN·meter (N = Newton) dN·meter minute minute dN·m/minute	ASTM D5289-95 (modified)

Table 2. Description of Components and Commercial Sources

Component	Description	Commercial Source
EXXPRO™ 3035	brominated poly(isobutylene-co-4-methylstyrene), 45±5 ML, 0.48±0.05 mol % Br, 5±1.5 wt % PMS.	ExxonMobil Chemical Co. (Houston, TX)
EXXPRO™ 96-4	brominated poly(isobutylene-co-4-methylstyrene), 44±5 ML, 0.85±0.05 mol% Br, 12±1.5 wt% PMS.	ExxonMobil Chemical Co. (Houston, TX)
Brominated vegetable oil	Inducer compound	Aldrich Chemical Co.
4-bromomethylbenzoic acid	Inducer compound	Aldrich Chemical Co.
4-bromomethylbenzophenone	Inducer compound	Aldrich Chemical Co.
1-bromonaphthalene	Inducer compound	Aldrich Chemical Co.
BUDENE™ 1207	cis-polybutadiene	Goodyear Chemical Company (Akron, OH)
Burgess 2211	Silane-treated clay	Burgess Pigment
CALSOL™ 810	Naphthenic Oil ASTM Type 103	R.E. Carroll, Inc (Trenton, NJ)
ESCOREZ™ 1102	Tackifying resin, melt viscosity 6000-8000 @ 140°C.	ExxonMobil Chemical Co. (Houston, TX)
Icecap K	Amine-treated clay	Burgess Pigment
Methyl α -bromophenylacetate	Inducer compound	Aldrich Chemical Co.
Octoate Z	Zinc-2-ethylhexanoate with petroleum processing oil	R.T. Vanderbilt Co., Inc.
SP-1045 Resin	phenol-formaldehyde resin	Schenectady International
SP-1055 Resin	Brominated phenol-formaldehyde resin	Schenectady International
SP-1068	Brominated phenol-formaldehyde resin	Schenectady International
Triphenylmethyl bromide	Inducer compound	Aldrich Chemical Co.

TABLE 3A. BIMS or polybutadiene for Example A.

Component (phr)	1	2	3	4	5	6
EXXPRO™ 3035	100	100	100	-	-	-
BUDENE™ 1207	-	-	-	100	100	100
N33 Carbon Black	60	60	60	60	60	60
Octoate Z	3	3	3	3	3	3
Triphenylmethyl bromide (TPMB)	-	3	-	-	3	-
4-bromomethylbenzophenone (BP)	-	-	3	-	-	3
Properties						
Scorch, s1 @ 135°C (min)	2.88	39.48	31.68	51.55	*	17.3
Scorch, s3 @ 135°C (min)	3.75	58.90	59.47	*	*	19.88
Cure, T ₉₀ @ 170°C (min)	1.13	0.65	1.86	16.66	3.69	2.42
T ₇₅ @ 170°C (min)	18.14	15.30	20.13	25.71	32.99	11.78
T ₉₀ @ 170°C (min)	27.58	34.23	37.42	44.04	48.29	27.40
MH-ML @ 170°C (dNm)	8.72	6.65	7.09	1.50	3.45	14.98
Peak Rate MDR @ 170°C (dNm/min)	1.46	2.73	1.23	0.43	0.87	1.93

* Did not reach in time allowed.

TABLE 3B. BIMS and polybutadiene blend of Example A.

Characteristic	No inducer	TPMB	BMBP
ML @ 170°C (dNm)	3.96	4.03	3.50
MH @ 170°C (dNm)	7.76	10.02	13.33
ML-MH @ 170°C (dNm)	3.80	5.99	9.83
T75 @ 170°C (min)	13.70	17.91	13.42
T90 @ 170°C (min)	27.75	38.92	32.66
Ts1 @ 170°C (min)	3.17	0.55	2.04
Peak Rate MDR @ 170°C (dNm/min)	0.70	8.62	1.08
S1, @ 135°C (min)	4.38	2.58	4.00
S3, @ 135°C (min)	5.13	3.10	7.28
S10, @ 135°C (min)	10.48	5.10	20.95

TABLE 4. BIMS and polybutadiene blend of Example B.

Component (phr)	1	2	3	4	5	6
Octoate Z	3	3	3	3	3	3
SP-1045	2	3	2	3	2	3
SP-1055	-	-	-	-	-	-
SP-1068	1.5	1.5	1.5	1.5	1.5	1.5
1-bromonaphthalene (BNAP)	2	2	-	-	-	-
4-bromobenzoic acid (BBA)	-	-	2	2	-	-
Methyl α -bromophenylacetate (MBPA)	-	-	-	-	2	2
Properties						
Scorch, s1 @ 135°C (min)	7.12	7.20	6.47	5.32	5.33	5.25
Scorch, s3 @ 135°C (min)	14.42	13.33	9.63	7.58	8.92	8.33
Cure, Ts1 @ 170°C (min)	2.96	2.68	2.22	1.98	1.49	1.40
T75@ 170°C (min)	21.35	22.11	16.65	17.41	11.44	8.94
T90@ 170°C (min)	35.47	36.22	29.82	31.21	23.70	17.02
MH-ML @ 170°C (dNm)	8.55	10.83	9.67	12.67	10.60	13.37
Peak Rate MDR @ 170°C (dNm/min)	0.48	0.52	0.68	0.86	1.21	1.81

TABLE 5. BIMS and polybutadiene blend of Example C.

Component (phr)	1	2	3	4	5	6	7	8	9	10
Octoate Z	3	3	3	3	3	3	3	3	3	3
SP-1045	-	-	-	2	3	2	3	2	3	2
SP-1055	2	3	4	-	-	-	-	-	-	-
SP-1068	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Triphenylmethyl bromide (TPMB)	-	-	-	2	2	-	-	-	-	-
4-bromomethylbenzophenone (BMBP)	-	-	-	-	-	2	2	-	-	-
Brominated vegetable oil (BVO)	-	-	-	-	-	-	-	2	2	-
Properties										
Scorch, s1 @ 135°C (min)	5.82	5.22	4.48	4.02	3.97	6.67	6.78	6.63	7.33	4.13
Scorch, s3 @ 135°C (min)	9.57	6.82	6.15	5.62	5.37	12.75	13.22	11.38	13.32	5.57
Scorch, s10 @ 135°C (min)	28.33	15.27	12.97	11.70	9.87	26.62	26.95	30.80	31.90	10.88
Cure, Tsl @ 170°C (min)	2.41	1.77	1.47	0.87	0.79	2.50	2.32	2.70	2.44	0.87
T75@ 170°C (min)	18.84	16.90	16.65	9.26	9.57	11.40	12.51	18.56	19.92	10.21
T90@ 170°C (min)	34.18	31.99	32.02	22.74	22.29	18.63	20.28	32.57	34.75	23.84
MH-ML @ 170°C (dNm)	8.32	11.80	14.35	10.28	12.89	12.69	14.86	9.39	11.60	11.69
Peak Rate MDR @ 170°C (dNm/min)	0.57	0.93	1.19	1.96	2.29	1.32	1.40	0.58	0.68	1.94

TABLE 6. BIMS (two levels of bromine) and Natural Rubber of Example D.

Component (phr)	1	2	3	4	5	6	7	8
EXXPRO™ 3035	-	-	-	-	35	35	35	35
EXXPRO™ 96-4	70	70	70	70	-	-	-	-
Burgess 2211	60	-	60	-	30	30	30	30
Icecap K	-	60	-	60	-	-	-	-
Octoate Z	3	3	3	3	3	3	3	3
SP-1045	-	-	3	3	2	2	3	3
SP-1055	3	3	-	-	-	-	-	-
4-bromomethylbenzoic acid	-	-	-	-	2	3	2	3
4-bromomethylbenzophenone	-	-	3	3	-	-	-	-
Properties								
Scorch, s1 @ 135°C (min)	11.03	12.08	10.55	11.70	13.33	18.33	13.95	16.48
Scorch, s3 @ 135°C (min)	20.00	20.05	17.77	18.38	23.58	31.20	24.43	26.90
Cure, Ts1 @ 170°C (min)	6.19	5.45	5.03	5.25	3.41	4.09	3.59	3.50
T75 @ 170°C (min)	32.12	36.17	32.88	34.09	17.12	18.26	17.80	17.26
T90 @ 170°C (min)	48.18	49.57	48.42	46.49	33.67	35.18	33.26	32.68
MH-ML @ 170°C (dNm)	3.67	4.63	4.12	5.28	4.19	3.81	5.03	4.98
Peak Rate MDR @ 170°C (dNm/min)	0.24	0.24	0.27	0.26	0.38	0.33	0.40	0.40

TABLE 7. BIMS and natural rubber blend of Example E.

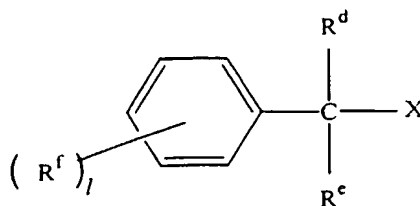
Component (phr)	1	2	3	4	5	6	7	8	9	10
SP-1045	-	-	-	2	3	2	3	2	3	2.5
SP-1055	2	3	4	-	-	-	-	-	-	-
Triphenylmethyl bromide (TPMB)	-	-	-	2	2	-	-	-	-	-
4-bromomethylbenzophenone (BMIBP)	-	-	-	-	-	2	2	-	-	-
Brominated vegetable oil (BVO)	-	-	-	-	-	-	-	2	2	-
Properties										
Scorch, s1 @ 135°C (min)	16.12	13.13	10.83	18.12	17.87	24.87	24.58	19.80	18.50	24.12
Scorch, s3 @ 135°C (min)	32.35	25.38	18.92	35.42	31.83	46.37	41.10	36.02	35.53	42.15
Scorch, s10 @ 135°C (min)	-	48.10	35.87	-	54.90	-	-	-	-	-
Cure, Ts1 @ 170°C (min)	6.72	4.50	3.98	5.05	3.92	6.28	5.32	7.80	5.86	5.43
T90 @ 170°C (min)	40.85	38.78	37.93	38.97	36.73	38.42	36.73	42.82	40.76	40.26
MH-ML @ 170°C (dNm)	2.94	4.05	4.55	3.68	4.88	3.38	4.53	3.38	4.72	4.05
Peak Rate MDR @ 170°C (dNm/min)	0.22	0.29	0.31	0.28	0.33	0.23	0.27	0.19	0.23	0.28

CLAIMS

We claim:

1. A method of curing an elastomer, the method comprising contacting:
 - (a) at least one uncured elastomer;
 - (b) at least one cure agent; and
 - (c) an inducer compound containing a dissociable or substitution labile halogen capable of transfer to the elastomer and/or the cure agent during curing;thus forming a blend; and maintaining the blend under conditions to effect the desired level of curing.
2. The method of Claim 1,
3. The method of Claim 1, the components are contacted at a temperature of from 25°C to 250°C to form a cured elastomeric composition.
4. The method of Claim 1, wherein the inducer compound possesses a tertiary, allylic or benzylic organohalogen functional group capable of transferring a halogen atom.
5. The method of Claim 1, wherein the inducer is represented by the following formula:

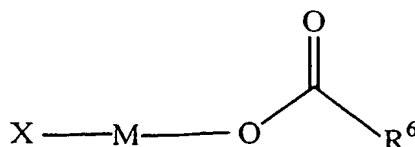
-50 -



wherein l is from 1 to 5, X is a halogen, R^d and R^e are the same or different and are selected from hydrogen, a C_1 to C_{26} straight, branched chain, and substituted alkyl, and a phenyl or substituted phenyl; and R^f is selected from the group consisting of a hydrogen atom, a C_1 - C_{10} alkyl group, a C_1 - C_{10} alkoxy group, a C_6 - C_{10} aryl group, a C_6 - C_{10} aryloxy group, a C_2 - C_{10} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_7 - C_{40} alkylaryl group, a C_8 - C_{40} arylalkenyl group, and a halogen atom.

6. The method of Claim 1, wherein the inducer is selected from a benzyl bromide (α -bromotoluene), 1-bromonaphthalene, 4-bromobenzoic acid, methyl α -bromophenylacetate, triphenylmethylbromide (bromotriphenylmethane), 4-bromomethylbenzophenone, brominated vegetable oil, 2-ethylhexylbromide, bromomethyl phenyl sulfone, 4-(bromomethyl)phenylacetic acid, 4-(trifluoromethyl)benzyl bromide, α^2 -chloroisodurene, 2-(chloromethyl)anthraquinone, 2,4-bis(trifluoromethyl)benzyl bromide, and mixtures thereof.

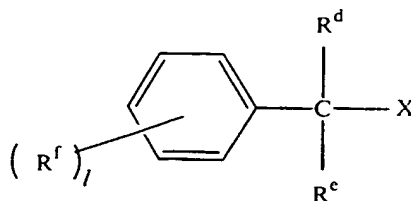
7. The method of Claim 1, wherein the cure agent is described by the following structure:



wherein X is a halogen, M is a Group 3-14 metal, and R⁶ is selected from a hydrogen and a C₁ to C₂₆ straight or branched chain alkyl, a substituted alkyl, and a substituted aryl.

- 5 8. The method of Claim 1, wherein the inducer is present from 0.1 to 20 phr.
9. The method of Claim 1, wherein the elastomer is selected from an unsaturated elastomer and a substituted phenylic elastomer.
- 10 10. The method of Claim 1, wherein the elastomer is selected from butyl rubber, natural rubber, polyisoprene, polybutadiene, poly(isobutylene-*co*-4-alkylstyrene), brominated poly(isobutylene-*co*-4-alkylstyrene), halogenated butyl rubber, and halogenated star-branched butyl rubber, poly(styrene-*co*-butadiene), polysulfide, nitrile rubber, propylene oxide
15 polymers and mixtures thereof.
11. The method of Claim 1, wherein the elastomer is a brominated poly(isobutylene-*co*-4-alkylstyrene).
- 20 12. The method of Claim 10, wherein the 4-alkylstyrene is 4-methylstyrene present from 3 wt% to 15 wt% of the copolymer.
13. The method of Claim 11, wherein from 0.20 mol% to 3.0 mol% of the copolymer comprises 4-bromomethylstyrene.
- 25 14. The method of Claim 1, wherein the at least one cure agent is a metal oxide or a metal ligand complex, or mixtures thereof.
15. The method of Claim 1, wherein the at least one cure agent further
30 comprises a non-halogenated phenolic resin.

16. The method of Claim 1, further comprising an additional component selected from natural rubber, butyl rubber, polybutadiene, polyisoprene, poly(styrene-*co*-butadiene), poly(styrene-isoprene-butadiene); poly(isobutylene-*co*-4-alkylstyrene), halogenated poly(isobutylene-*co*-4-methylstyrene), halogenated butyl rubber, star-branched butyl rubber, halogenated star-branched butyl rubber, polyethylene, polypropylene, polypropylene copolymers and impact copolymers, ethylene-propylene rubber, polysulfide, nitrile rubber, propylene oxide polymer, acrylates and acetates, star-branched butyl rubber, nylons, thermoplastic resins, polyisobutylene and mixtures thereof.
17. A component of a tire produced according to the method of Claim 1.
18. An elastomeric composition comprising:
- (a) at least one uncured elastomer; and
 - (b) an inducer compound capable of transferring a halogen species to a secondary agent selected from the uncured elastomer, a cure agent, and blends thereof.
19. The composition of Claim 17,
20. The composition of Claim 18, wherein the inducer compound possesses a tertiary, allylic or benzylic organohalogen functional group capable of transferring a halogen atom.
21. The composition of Claim 18, wherein the inducer is described by the following formula:

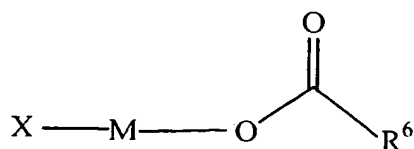


wherein *l* is from 1 to 5, X is a halogen, R^d and R^e are the same or different and are selected from hydrogen, a C₁ to C₂₆ straight, branched chain, and substituted alkyl, and a phenyl or substituted phenyl; and R^f is selected from the group consisting of a hydrogen atom, a C₁-C₁₀ alkyl group, a C₁-C₁₀ alkoxy group, a C₆-C₁₀ aryl group, a C₆-C₁₀ aryloxy group, a C₂-C₁₀ alkenyl group, a C₇-C₄₀ arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, and a halogen atom.

22. The composition of Claim 18, wherein the inducer is selected from a benzyl bromide (α -bromotoluene), 1-bromonaphthalene, 4-bromobenzoic acid, methyl α -bromophenylacetate, triphenylmethylbromide (bromotriphenylmethane), 4-bromomethylbenzophenone, brominated vegetable oil, 2-ethylhexylbromide, bromomethyl phenyl sulfone, 4-(bromomethyl)phenylacetic acid, 4-(trifluoromethyl)benzyl bromide, α^2 -chloroisodurene, 2-(chloromethyl)anthraquinone, 2,4-bis(trifluoromethyl)benzyl bromide, and mixtures thereof.
23. The composition of Claim 18, wherein the inducer is present from 0.1 to 20 phr.
24. The composition of Claim 18, wherein the elastomer is selected from an unsaturated elastomer and a substituted phenylic elastomer.
25. The composition of Claim 18, wherein the elastomer is selected from butyl rubber, natural rubber, poly(styrene-*co*-butadiene), polyisoprene, polybutadiene, poly(isobutylene-*co*-4-alkylstyrene), brominated

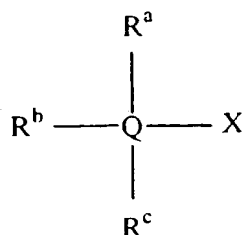
poly(isobutylene-*co*-4-alkylstyrene), halogenated butyl rubber, and halogenated star-branched butyl rubber, polysulfide, nitrile rubber, propylene oxide polymers and mixtures thereof.

- 5 26. The composition of Claim 18, wherein the elastomer is a brominated poly(isobutylene-*co*-4-alkylstyrene).
27. The composition of Claim 26, wherein the 4-alkylstyrene is 4-methylstyrene present from 3 wt% to 15 wt% of the copolymer.
- 10 28. The composition of Claim 26, wherein from 0.20 mol% to 3.0 mol% of the copolymer comprises 4-bromomethylstyrene.
29. The composition of Claim 26, wherein the brominated poly(isobutylene-*co*-4-alkylstyrene) is present in the composition from 10 to 100 phr.
- 15 30. The composition of Claim 18, wherein the inducer compound is present from 0.1 to 20 phr.
31. The composition of Claim 18, further comprising at least one cure agent.
- 20 32. The composition of Claim 31, wherein the at least one cure agent is a metal oxide or a metal ligand complex, or mixtures thereof.
33. The composition of Claim 31, wherein the cure agent is present from 0.1 to 10 phr.
- 25 34. The composition of Claim 31, wherein the at least one cure agent also comprises a non-halogenated phenolic resin.
35. The composition of Claim 31, wherein the cure agent is described by the following structure:
- 30



wherein X is a halogen, M is a Group 3-14 metal, and R⁶ is selected from a hydrogen and a C₁ to C₂₆ straight or branched chain alkyl, a substituted alkyl, and a substituted aryl.

36. The composition of Claim 17, further comprising an additional component selected from natural rubber, butyl rubber, polybutadiene, polyisoprene, poly(styrene-*co*-butadiene), poly(styrene-isoprene-butadiene); poly(isobutylene-*co*-4-alkylstyrene), halogenated poly(isobutylene-*co*-4-methylstyrene), halogenated butyl rubber, star-branched butyl rubber, halogenated star-branched butyl rubber, polyethylene, polypropylene, polypropylene copolymers and impact copolymers, ethylene-propylene rubber, polysulfide, nitrile rubber, propylene oxide polymer, acrylates and acetates, star-branched butyl rubber, nylons, thermoplastic resins, polyisobutylene and mixtures thereof.
37. The composition of Claim 17, wherein the composition is formed into a tire component.
38. A method of curing an elastomer, the method comprising contacting the following:
 - (a) at least one uncured elastomer;
 - (b) an inducer, wherein the inducer is represented by the following formula:



wherein Q is selected from carbon, silicon, and germanium; X is a halogen; and R^a , R^b and R^c are the same or different and are selected from hydrogen, a C_1 to C_{20} alkyl, a C_1 to C_{20} substituted alkyl, aryl, and substituted aryl; and

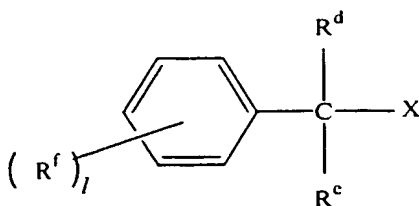
(c) at least one cure agent.

39. The method of Claim 38, the components are contacted at a temperature of from 25°C to 250°C to form a cured elastomeric composition.

40. The method of Claim 38, wherein the inducer compound possesses a tertiary, allylic or benzylic organohalogen functional group capable of transferring a halogen atom.

15

41. The method of Claim 38, wherein the inducer is represented by the following formula:



20

wherein l is from 1 to 5, X is a halogen, R^d and R^c are the same or different and are selected from hydrogen, a C_1 to C_{26} straight, branched chain, and substituted alkyl, and a phenyl or substituted phenyl; and R^f is selected

from a hydrogen atom, a C₁-C₁₀ alkyl group, a C₁-C₁₀ alkoxy group, a C₆-C₁₀ aryl group, a C₆-C₁₀ aryloxy group, a C₂-C₁₀ alkenyl group, a C₇-C₄₀ arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, and a halogen atom.

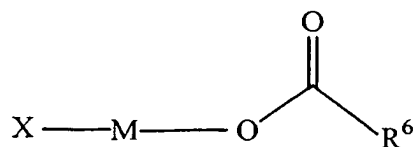
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42. The method of Claim 38, wherein the inducer is selected from a benzyl bromide (α -bromotoluene), 1-bromonaphthalene, 4-bromobenzoic acid, methyl α -bromophenylacetate, triphenylmethylbromide (bromotriphenylmethane), 4-bromomethylbenzophenone, brominated vegetable oil, 2-ethylhexylbromide, bromomethyl phenyl sulfone, 4-(bromomethyl)phenylacetic acid, 4-(trifluoromethyl)benzyl bromide, α^2 -chloroisodurene, 2-(chloromethyl)anthraquinone, 2,4-bis(trifluoromethyl)benzyl bromide, and mixtures thereof.

10

43. The method of Claim 38, wherein the cure agent is described by the following structure:

15



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wherein X is a halogen, M is a Group 3-14 metal, and R⁶ is selected from a hydrogen and a C₁ to C₂₆ straight or branched chain alkyl, a substituted alkyl, and a substituted aryl.

25

44. The method of Claim 38, wherein the inducer is present from 0.1 to 20 phr.
45. The method of Claim 38, wherein the elastomer is selected from an unsaturated elastomer and a substituted phenylic elastomer.

46. The method of Claim 38, wherein the elastomer is selected from butyl rubber, natural rubber, polyisoprene, polybutadiene, poly(isobutylene-*co*-4-alkylstyrene), brominated poly(isobutylene-*co*-4-alkylstyrene), halogenated butyl rubber, and halogenated star-branched butyl rubber, poly(styrene-*co*-butadiene), polysulfide, nitrile rubber, propylene oxide polymers and mixtures thereof.
47. The method of Claim 38, wherein the elastomer is a brominated poly(isobutylene-*co*-4-alkylstyrene).
48. The method of Claim 47, wherein the 4-alkylstyrene is 4-methylstyrene present in the copolymer from 4 wt% to 15 wt% of the copolymer.
49. The method of Claim 47, wherein from 0.20 mol% to 3.0 mol% of the brominated poly(isobutylene-*co*-4-alkylstyrene) comprises 4-bromomethylstyrene.
50. The method of Claim 38, wherein the at least one cure agent is a metal oxide or a metal ligand complex, or mixtures thereof.
51. The method of Claim 38, wherein the at least one cure agent further comprises a non-halogenated phenolic resin.
52. The method of Claim 38, further comprising an additional component selected from natural rubber, butyl rubber, polybutadiene, polyisoprene, poly(styrene-*co*-butadiene), poly(styrene-isoprene-butadiene); poly(isobutylene-*co*-4-alkylstyrene), halogenated poly(isobutylene-*co*-4-methylstyrene), halogenated butyl rubber, star-branched butyl rubber, halogenated star-branched butyl rubber, polyethylene, polypropylene, polypropylene copolymers and impact copolymers, ethylene-propylene rubber, polysulfide, nitrile rubber, propylene oxide polymer, acrylates and

acetates, star-branched butyl rubber, nylons, thermoplastic resins, polyisobutylene and mixtures thereof.

53. A component of a tire produced according to the method of Claim 38.

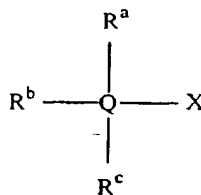
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54. An elastomeric composition comprising:

(a) at least one uncured elastomer; and

10

(b) an inducer compound, wherein the inducer is described by the following:



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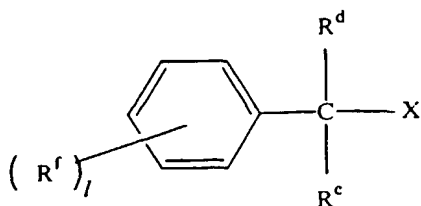
wherein Q is selected from carbon, silicon, or germanium; X is a halogen; and R^a , R^b and R^c are the same or different and are selected from hydrogen, a C_1 to C_{20} alkyl, a C_1 to C_{20} substituted alkyl, aryl, or substituted aryl.

20

55. The composition of Claim 54, wherein the inducer compound possesses a tertiary, allylic or benzylic organohalogen functional group capable of transferring a halogen atom.

56. The composition of Claim 54, wherein the inducer is described by the following:

-60 -



wherein l is from 1 to 5, X is a halogen, R^d and R^e are the same or different and are selected from hydrogen, a C_1 to C_{26} straight, branched chain, and substituted alkyl, and a phenyl or substituted phenyl; and R^f is selected from the group consisting of a hydrogen atom, a C_1 - C_{10} alkyl group, a C_1 - C_{10} alkoxy group, a C_6 - C_{10} aryl group, a C_6 - C_{10} aryloxy group, a C_2 - C_{10} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_7 - C_{40} alkylaryl group, a C_8 - C_{40} arylalkenyl group, and a halogen atom.

57. The composition of Claim 54, wherein the inducer is selected from benzyl bromide (α -bromotoluene), α -chlorotoluene, 1-bromonaphthalene, 1-chloronaphthalene, 4-bromobenzoic acid, 4-chlorobenzoic acid, methyl α -bromophenylacetate, methyl α -chlorophenylacetate, triphenylmethylbromide (bromotriphenylmethane), chlorotriphenylmethane, diphenylmethylbromide, diphenylmethylchloride, (3-bromopropyl)benzene, 4-bromomethylbenzophenone, brominated vegetable oil, chlorinated vegetable oil, 2-ethylhexylbromide, 2-ethylhexylchloride, bromomethyl phenyl sulfone, 4-(bromomethyl)phenylacetic acid, 4-methylbenzylbromide, 2-bromo-2-methylpropane, 2-chloro-2-methylpropane, 4-methylbenzylchloride, 2-methylbenzylbromide, 2-methylbenzylchloride, 1-bromo-3-(bromomethyl)adamantane, 1-bromoadamantane, bromobornane, chlorobornane, 9-bromophenanthrene, bromophenol blue (3',3'',5',5''-tetrabromophenolsulfonephthalein sodium salt), 9-bromofluorene, 4-bromophenol, 4-(trifluoromethyl)benzyl bromide, α^2 -chloroisodurene, 2-(chloromethyl)anthraquinone, and 2,4-bis(trifluoromethyl)benzyl bromide, and blends thereof.

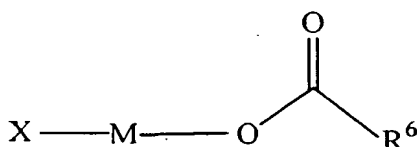
58. The composition of Claim 54, wherein the inducer is present from 0.1 to 20 phr.
- 5 59. The composition of Claim 54, wherein the elastomer is selected from an unsaturated elastomer and a substituted phenylic elastomer.
60. The composition of Claim 54, wherein the elastomer is selected from butyl rubber, natural rubber, poly(styrene-*co*-butadiene), polyisoprene,
10 polybutadiene, poly(isobutylene-*co*-4-alkylstyrene), brominated poly(isobutylene-*co*-4-alkylstyrene), halogenated butyl rubber, and halogenated star-branched butyl rubber, polysulfide, nitrile rubber, propylene oxide polymers and mixtures thereof.
- 15 61. The composition of Claim 54, wherein the elastomer is a brominated poly(isobutylene-*co*-4-alkylstyrene) elastomer.
62. The composition of Claim 61, wherein the 4-alkylstyrene is 4-methylstyrene present from 4 wt% to 15 wt% of the copolymer.
- 20 63. The composition of Claim 61, wherein from 0.20 mol% to 3.0 mol% of the brominated poly(isobutylene-*co*-4-alkylstyrene) is 4-bromomethylstyrene.
64. The composition of Claim 54, wherein the brominated poly(isobutylene-
25 *co*-4-alkylstyrene) is present in the composition from 10 to 100 phr.
65. The composition of Claim 54, wherein the inducer compound is present from 0.1 to 20 phr.
- 30 66. The composition of Claim 54, further comprising at least one cure agent.

67. The composition of Claim 66, wherein the at least one cure agent is a metal oxide or a metal ligand complex, or mixtures thereof.

68. The composition of Claim 66, wherein the cure agent is present from 0.1 to 10 phr.

69. The composition of Claim 66, wherein the at least one cure agent also comprises a non-halogenated phenolic resin.

70. The composition of Claim 66, wherein the at least one cure agent is described by the following structure:



wherein X is a halogen, M is a Group 3-14 metal, and R⁶ is selected from a hydrogen and a C₁ to C₂₆ straight or branched chain alkyl, a substituted alkyl, and a substituted aryl.

71. The composition of Claim 54, further comprising an additional component selected from natural rubber, butyl rubber, polybutadiene, polyisoprene, poly(styrene-*co*-butadiene), poly(styrene-isoprene-butadiene); poly(isobutylene-*co*-4-alkylstyrene), halogenated poly(isobutylene-*co*-4-methylstyrene), halogenated butyl rubber, star-branched butyl rubber, halogenated star-branched butyl rubber, polyethylene, polypropylene, polypropylene copolymers and impact copolymers, ethylene-propylene rubber, polysulfide, nitrile rubber, propylene oxide polymer, acrylates and acetates, star-branched butyl rubber, nylons, thermoplastic resins, polyisobutylene and mixtures thereof.

72. The composition of Claim 54, wherein the composition is formed into a tire component.

5 73. The use in a method of curing an elastomer with a cure agent and an inducer compound containing a dissociable or substitution labile halogen capable of transfer to the uncured elastomer and/or the cure agent during curing.

10 74. A method of forming a component in an vehicle tire and/or air barrier comprising contacting:

(a) at least one uncured elastomer;

15 (b) at least one cure agent; and

(c) an inducer compound containing a dissociable or substitution labile halogen capable of transfer to the elastomer and/or the cure agent during curing;

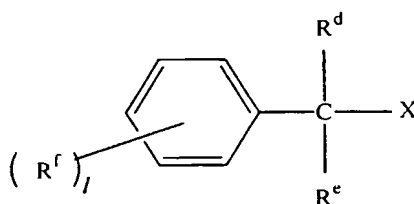
20 thus forming a blend; and maintaining the blend under conditions to effect the desired level of curing.

25 75. The method of Claim 74, wherein the components are contacted at a temperature of from 25°C to 250°C to form a cured elastomeric composition.

30 76. The method of Claim 74, wherein the components are contacted at a temperature of from 25°C to the melting point of the elastomer to form a cured elastomeric composition.

77. The method of Claim 74, wherein the inducer compound possesses a tertiary, allylic or benzylic organohalogen functional group capable of transferring a halogen atom.

5 78. The method of Claim 74, wherein the inducer is represented by the following formula:



10 wherein l is from 1 to 5, X is a halogen, R^d and R^e are the same or different and are selected from hydrogen, a C_1 to C_{26} straight, branched chain, and substituted alkyl, and a phenyl or substituted phenyl; and R^f is selected from the group consisting of a hydrogen atom, a C_1 - C_{10} alkyl group, a C_1 - C_{10} alkoxy group, a C_6 - C_{10} aryl group, a C_6 - C_{10} aryloxy group, a C_2 - C_{10} alkenyl group, a C_7 - C_{40} arylalkyl group, a C_7 - C_{40} alkylaryl group, a C_8 - C_{40} arylalkenyl group, and a halogen atom.

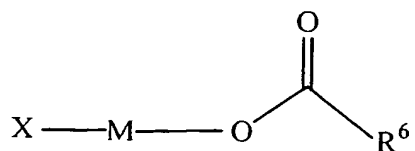
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79. The method of Claim 74, wherein the inducer is selected from a benzyl bromide (α -bromotoluene), 1-bromonaphthalene, 4-bromobenzoic acid, methyl α -bromophenylacetate, triphenylmethylbromide (bromotriphenylmethane), 4-bromomethylbenzophenone, brominated vegetable oil, 2-ethylhexylbromide, bromomethyl phenyl sulfone, 4-(bromomethyl)phenylacetic acid, 4-(trifluoromethyl)benzyl bromide, α^2 -chloroisodurene, 2-(chloromethyl)anthraquinone, 2,4-bis(trifluoromethyl)benzyl bromide, and mixtures thereof.

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80. The method of Claim 74, wherein the cure agent is described by the following structure:



wherein X is a halogen, M is a Group 3-14 metal, and R⁶ is selected from a hydrogen and a C₁ to C₂₆ straight or branched chain alkyl, a substituted alkyl, and a substituted aryl.

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81. The method of Claim 74, wherein the inducer is present from 0.1 to 20 phr.

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82. The method of Claim 74, wherein the elastomer is selected from an unsaturated elastomer and a substituted phenylic elastomer.

15

83. The method of Claim 74, wherein the elastomer is selected from butyl rubber, natural rubber, polyisoprene, polybutadiene, poly(isobutylene-co-4-alkylstyrene), brominated poly(isobutylene-co-4-alkylstyrene), halogenated butyl rubber, and halogenated star-branched butyl rubber, poly(styrene-co-butadiene), polysulfide, nitrile rubber, propylene oxide polymers and mixtures thereof.

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84. The method of Claim 83, wherein the elastomer is a brominated poly(isobutylene-co-4-alkylstyrene).

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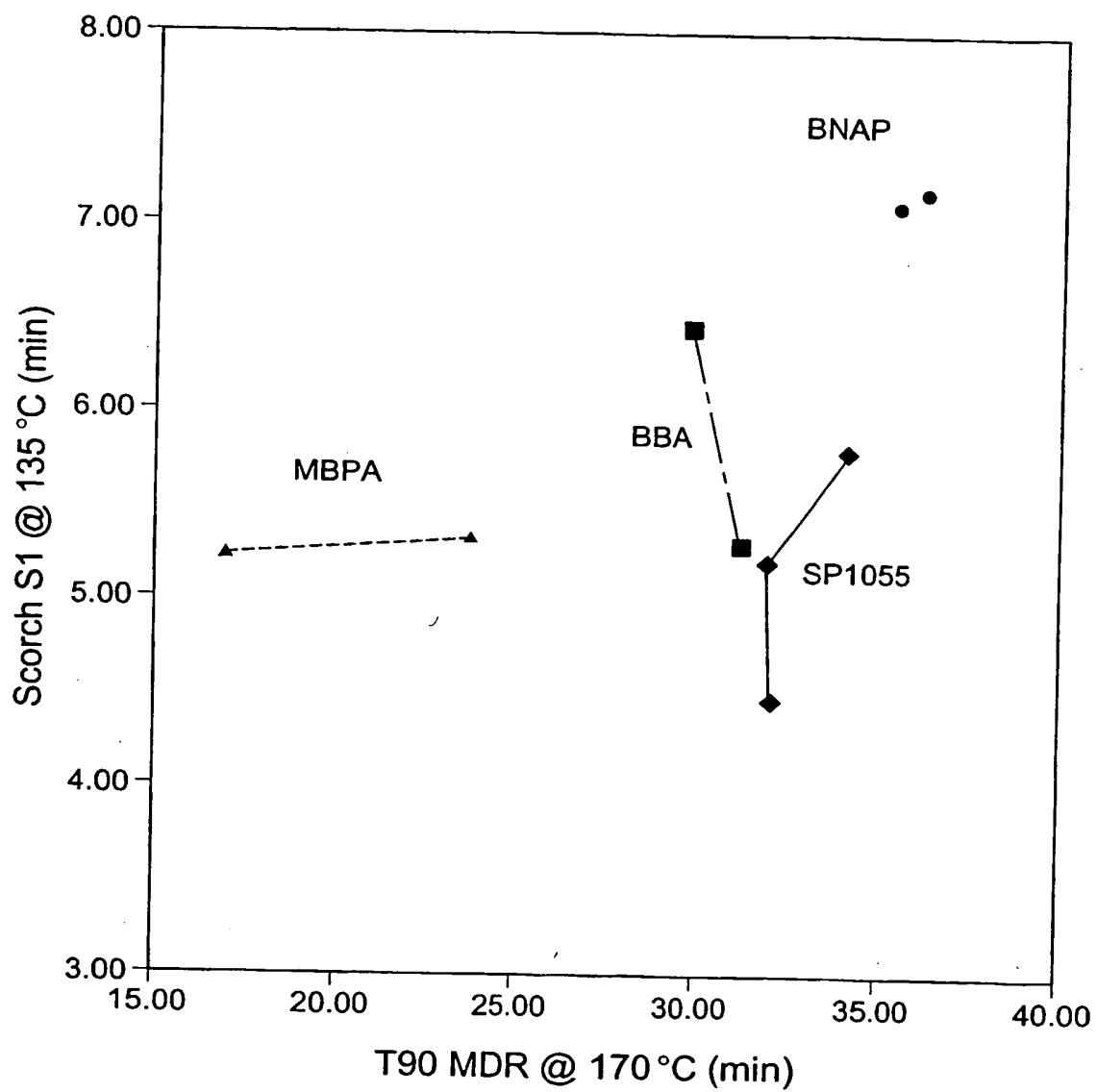
85. The method of Claim 84, wherein the 4-alkylstyrene is 4-methylstyrene present in the copolymer from 4 wt% to 15 wt% of the copolymer.

86. The method of Claim 83, wherein from 0.20 mol% to 3.0 mol% of the brominated poly(isobutylene-co-4-alkylstyrene) comprises 4-bromomethylstyrene.

87. The method of Claim 74, wherein the at least one cure agent is a metal oxide or a metal ligand complex, or mixtures thereof.
88. The method of Claim 74, wherein the at least one cure agent further
5 comprises a non-halogenated phenolic resin.
89. The method of Claim 74, wherein halogenated phenolic resins are substantially absent.
- 10 90. The method of Claim 74, further comprising an additional component selected from natural rubber, butyl rubber, polybutadiene, polyisoprene, poly(styrene-*co*-butadiene), poly(styrene-isoprene-butadiene); poly(isobutylene-*co*-4-alkylstyrene), halogenated poly(isobutylene-*co*-4-methylstyrene), halogenated butyl rubber, star-branched butyl rubber,
15 halogenated star-branched butyl rubber, polyethylene, polypropylene, polypropylene copolymers and impact copolymers, ethylene-propylene rubber, polysulfide, nitrile rubber, polycarbonate, propylene oxide polymer, acrylates and acetates, star-branched butyl rubber, nylons, thermoplastic resins, polyisobutylene and mixtures thereof.
- 20 91. An vehicle tire innerliner, sidewall, tread or air bladder made by the method of Claim 74.

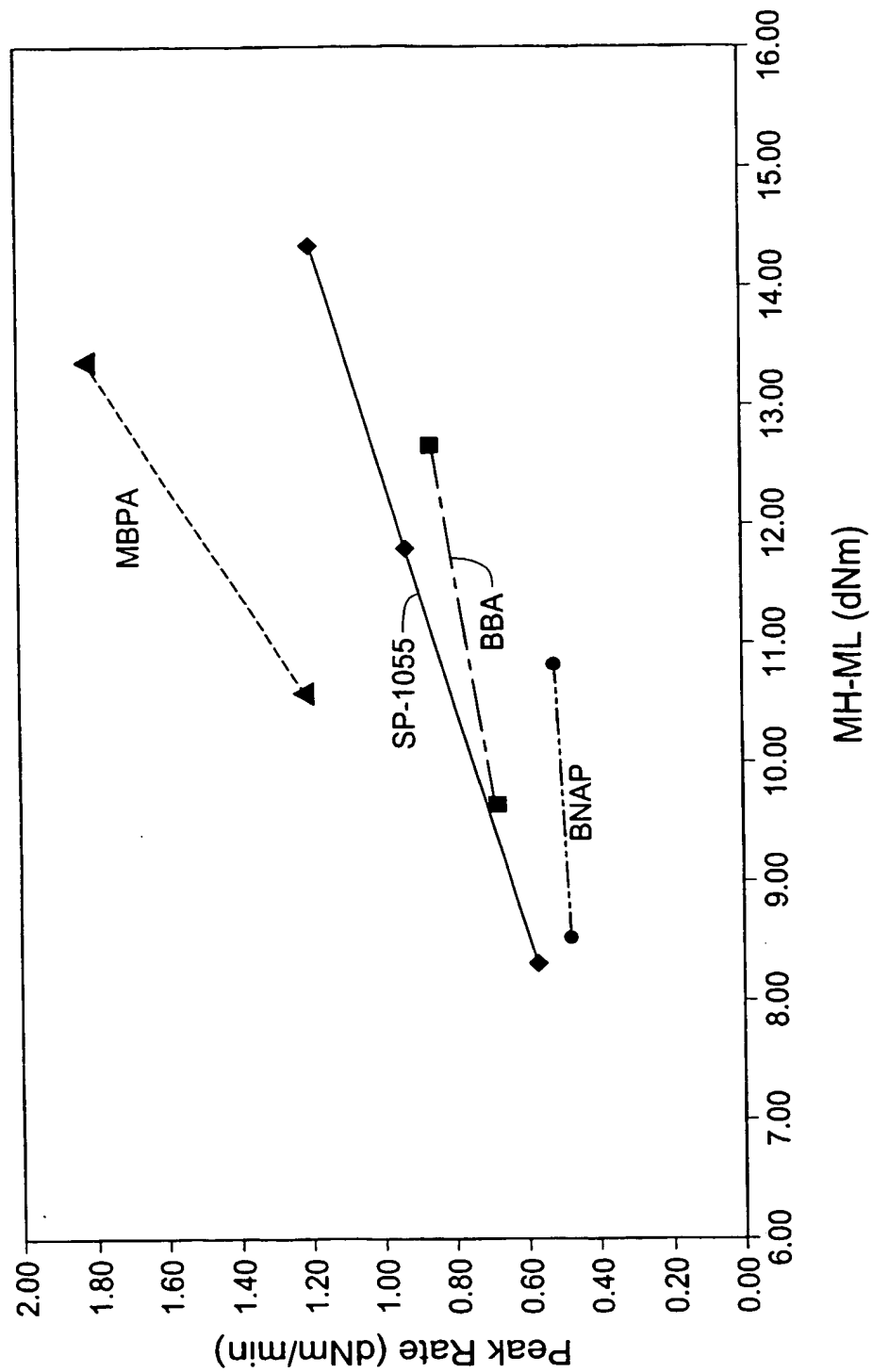
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Fig. 1



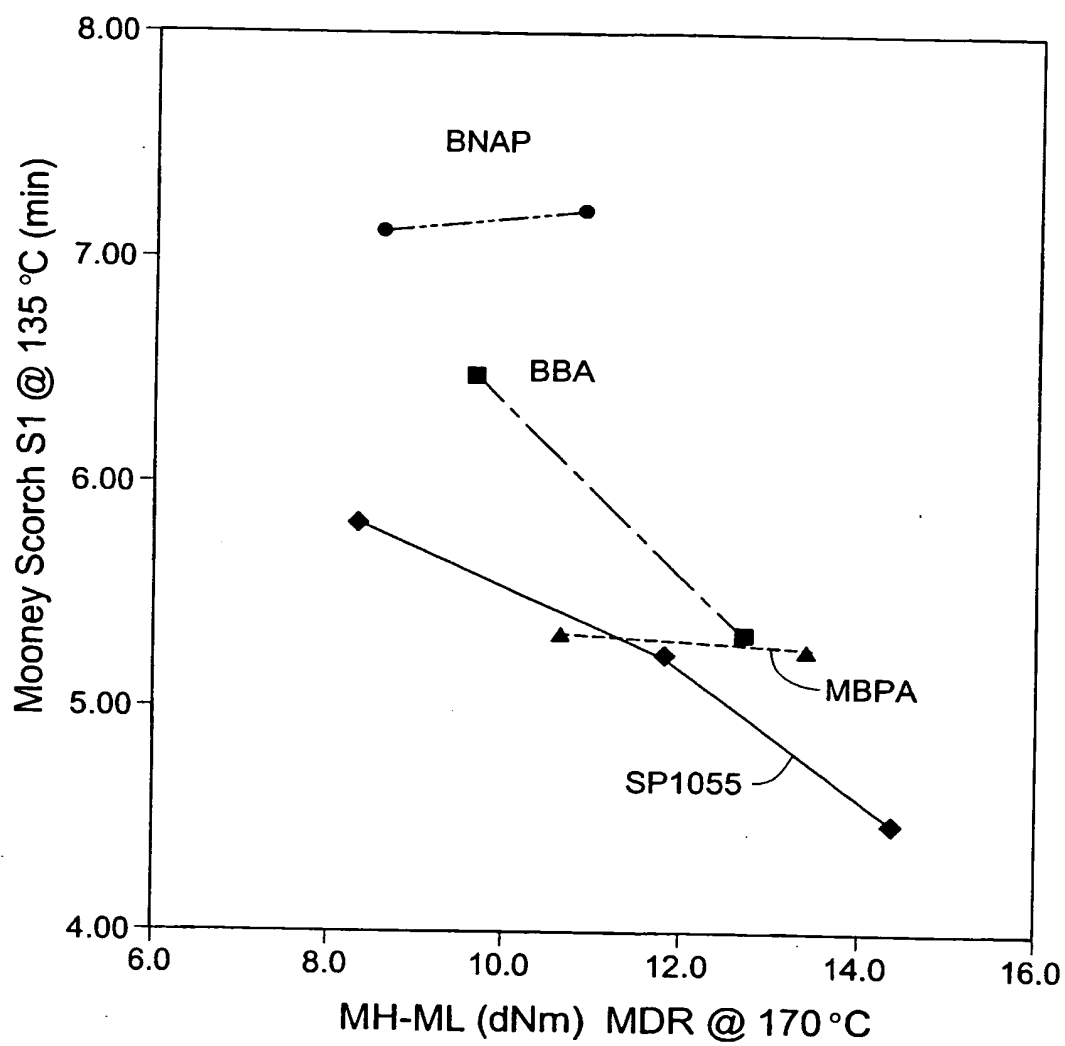
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Fig. 2



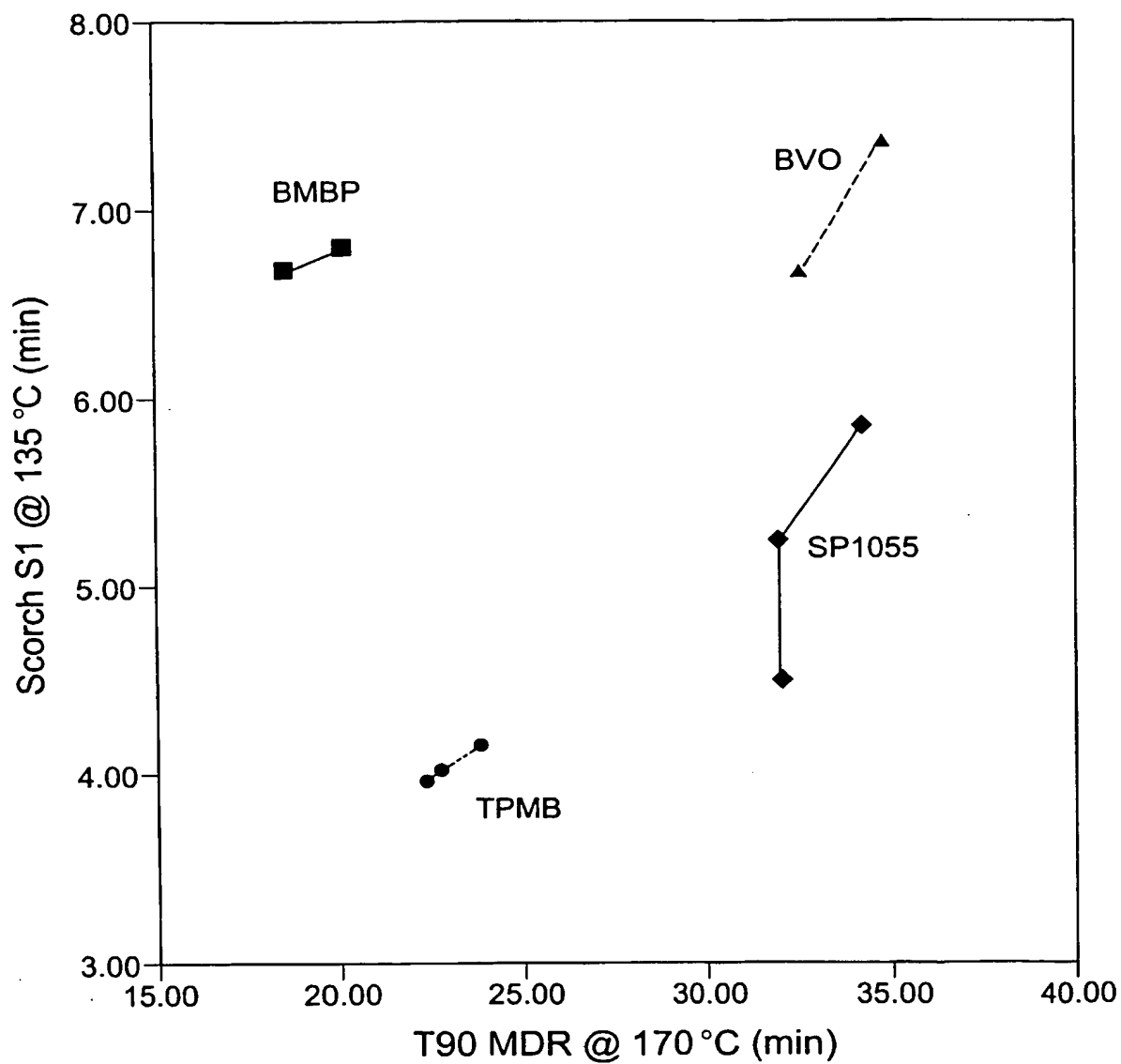
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Fig. 3



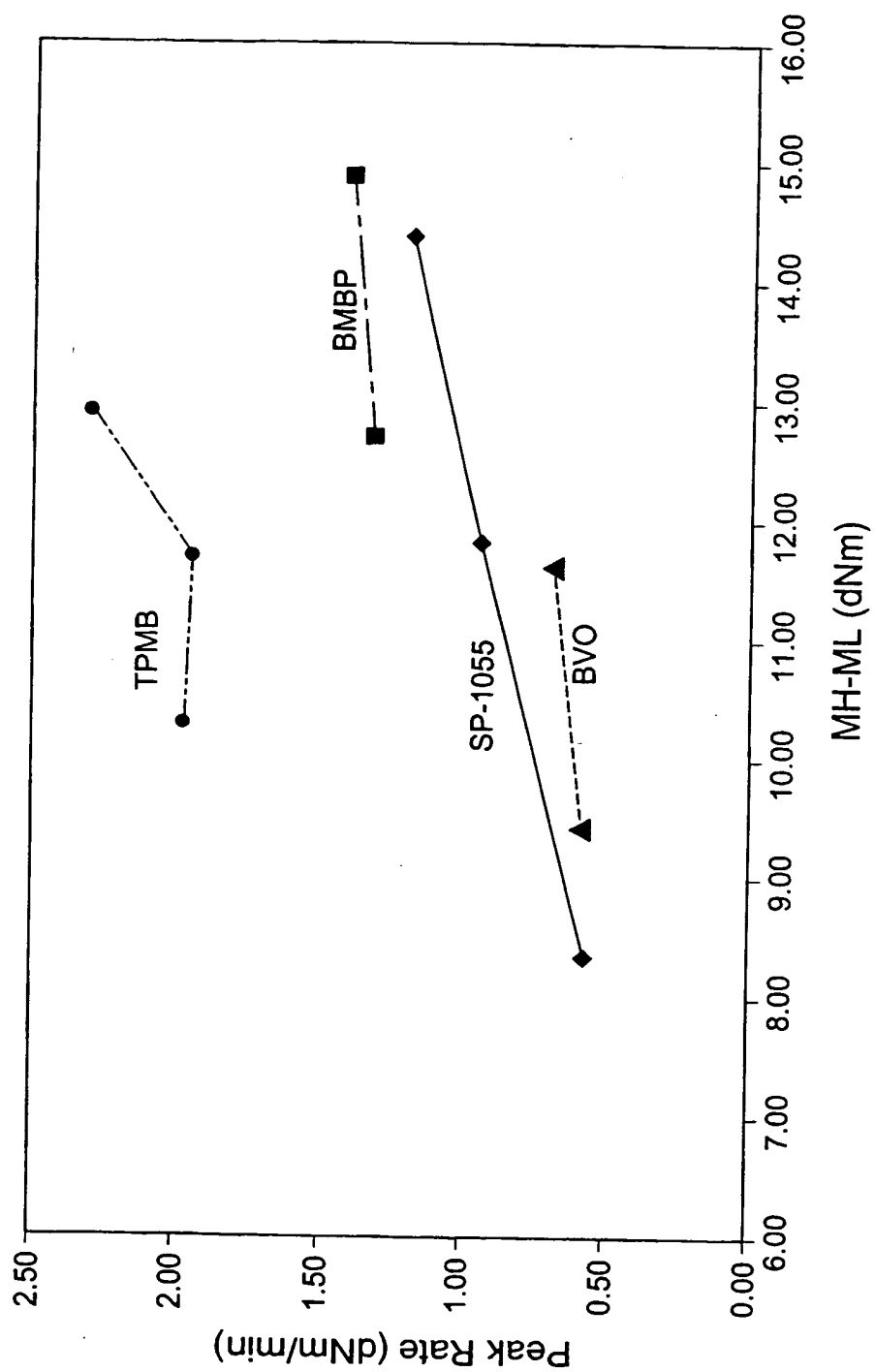
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Fig. 4



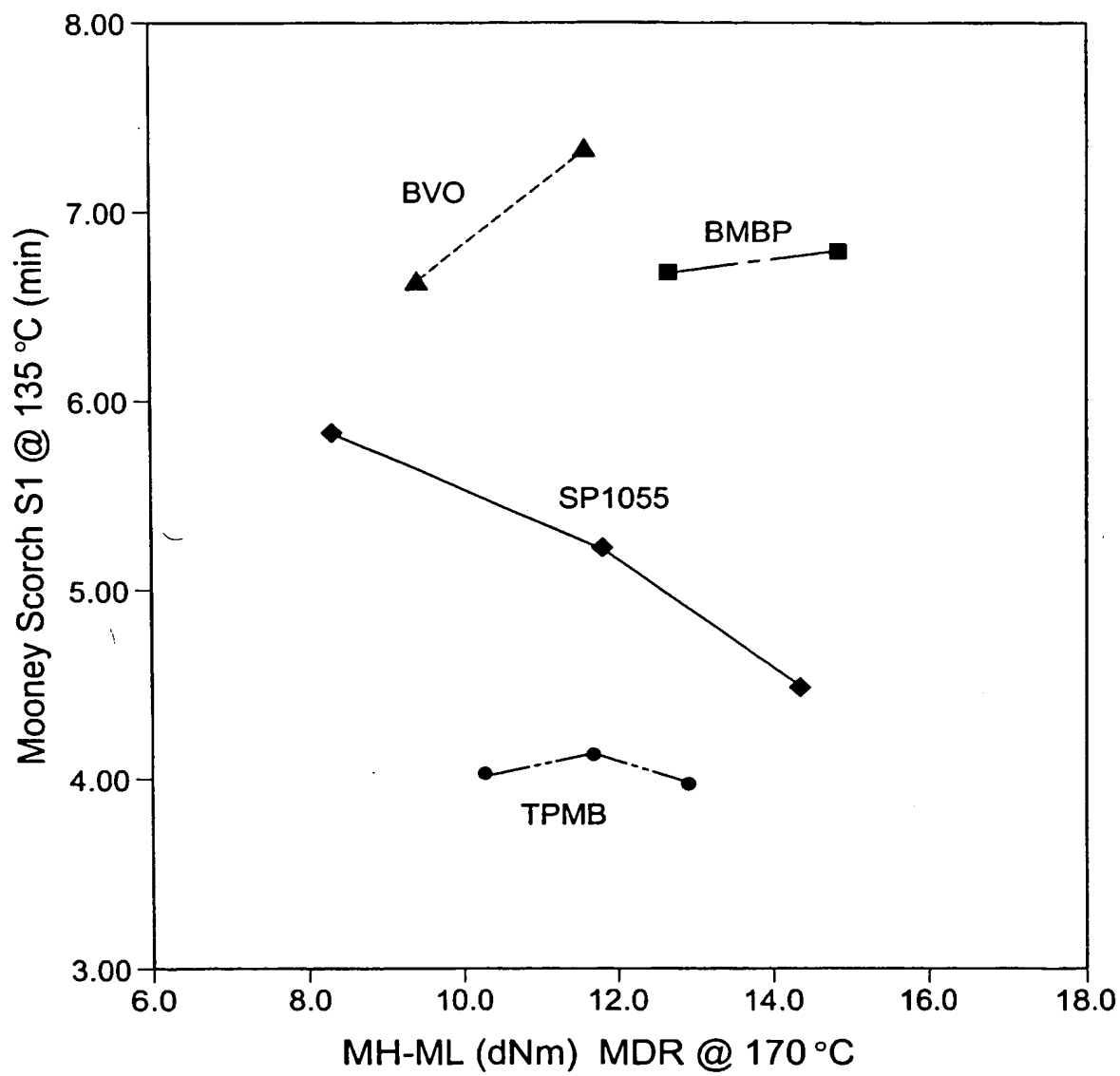
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Fig. 5



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Fig. 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/11548**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : C08F 8/18

US CL : 525/332.8, 332.9, 333.1, 333.2, 359.1, 359.4, 359.6

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/332.8, 332.9, 333.1, 333.2, 359.1, 359.4, 359.6

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,916,957 A (ITOH et al.) 29 June 1999.	1-91
A	US 4,935,471 A (HALASA et al.) 19 June 1990.	1-91
A	US 4,927,887 A (TATE et al.) 22 May 1990.	1-91
A	US 4,742,124 A (TSUTSUMI et al.) 03 May 1988.	1-91
A	US 4,482,678 A (FURUKAWA et al.) 13 November 1984.	1-91

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

27 JUNE 2002

Date of mailing of the international search report

12 JUL 2002

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